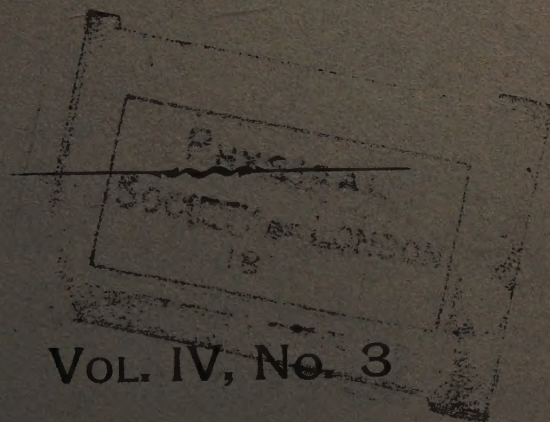


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On the Beckmann Rearrangement. IX.

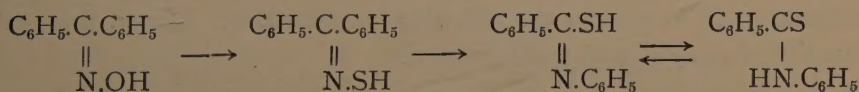
Action of Phosphorus Pentasulphide upon Benzophenoxime.

BY

Mitsuru Kuhara and Kôzô Kashima.

(Received June 27, 1919)

Dodge¹ states that he has obtained thiobenzanilide by the action of phosphorus pentasulphide upon the warm benzene solution of benzophenoxime, assuming that the reaction would be analogous to the Beckmann rearrangement. Also Ciusa² has conducted the similar experiment, expecting to prepare thiobenzophenoxime by the action of phosphorus pentasulphide upon the carbon bisulphide solution of benzophenoxime, but not succeeded to isolate the substance expected, while thiobenzanilide has been observed to be produced. He has, therefore, ascribed the reaction likewise to the Beckmann rearrangement of thiobenzophenoxime which is supposed to be formed in the intermediate stage of reaction, its primary cause being possibly due to the more acidic nature of sulphur than oxygen³; the scheme of reaction has been proposed as follows:



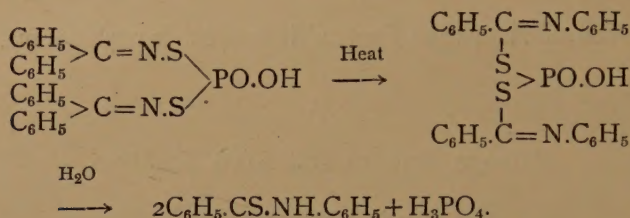
The authors have, however, noticed that the formation of thiobenzanilide from benzophenoxime by phosphorus pentasulphide may not be due to the direct rearrangement of thiobenzophenoxime, but seems to be dependent upon the rearrangement of a phosphoryl ester of

¹ Dodge, Lieb. Ann. 264, 184 (1891).

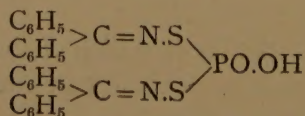
² Ciusa, Chem. Centralbl., 1907, I, 28.

³ Sidgiwick, Org. Chem. of Nitrogen, (1910), p.89.

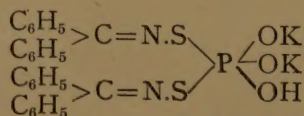
thiobenzophenoxime which is possible to be formed as an intermediate product, just as one of us (M.K.) and his collaborators have ever noticed in the rearrangement of the acylesters of ketoximes, that is, standing in harmony with Kuhara's theory of migration of the negative acyloxyl radicals,¹ the scheme of rearrangement being represented as follows :



In the authors' experiment, benzophenoxime and phosphorus pentasulphide were allowed to act upon each other in proportion of 5 mols and 1 mol respectively with the addition of $1\frac{1}{2}$ mols phosphorus pentoxide, ether having been selected as solvent in order to keep the temperature of the mixture so low as to its boiling point (35°), while Dodge took benzene (boil. pt. 80°), and Ciusa carbon bisulphide (boil. pt. 46°). Driving off ether by passing the current of dry air through the ethereal solution, greenish yellow substance of fibrous structure was left as a residue, which by a slight elevation of temperature undergoes rearrangement with explosive violence. On account of such an explosive nature of the substance it was highly difficult to get in a perfectly pure state; so the substance was treated with alcoholic potash, by which process a substance consisting of white crystalline powder was obtained and purified by the repeated recrystallization from ethyl acetate. This substance also undergoes rearrangement at 149° , but not so violently as the yellow substance. Consequently, the yellow and white substances seem to possess the following constitutions, inferred from the results of analysis and their properties :



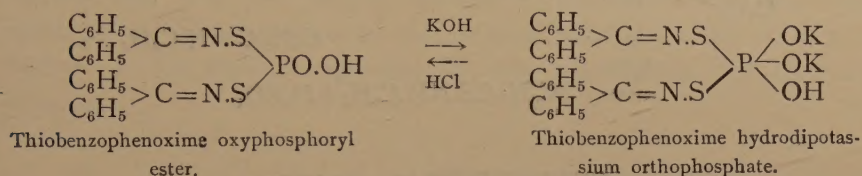
Greenish yellow fibrous substance.



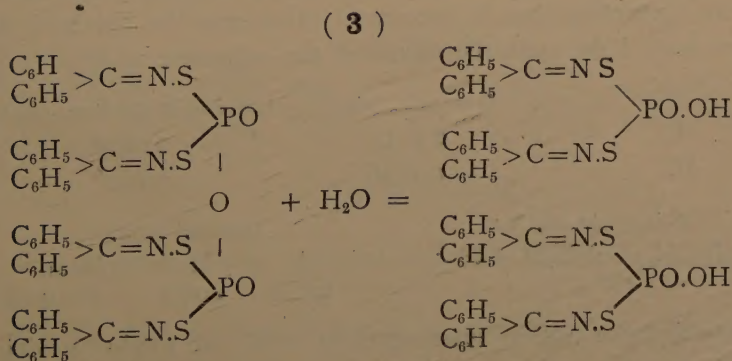
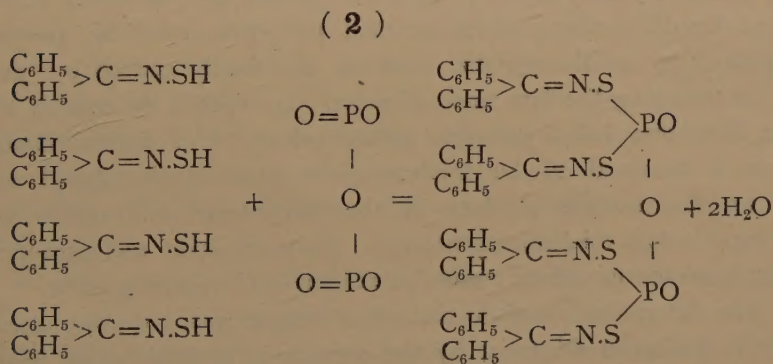
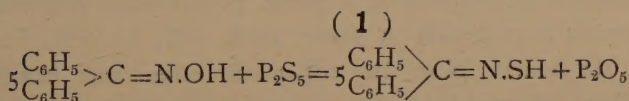
White crystalline substance.

¹ Kuhara, and Kainosho, Mem.Coll. Sci. Eng., Kyoto, 1, 254 (1903-1908); Kuhara and Todo, Ibid., 2, 387 (1909-1910); Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914); Kuhara and Watanabe: Ibid., 1, 349 (1916); Kuhara and Ishikawa: Ibid., 355 (1916); Kuhara, Agatsuma and Araki, Ibid., 3, 1 (1917).

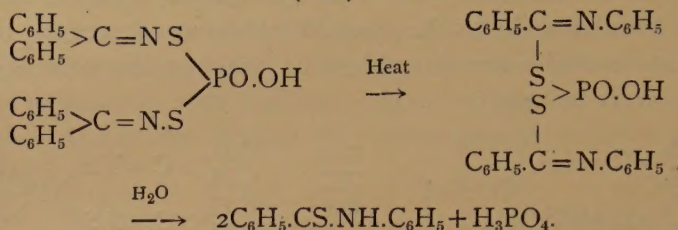
The white substance, on treating with hydrochloric acid, was found to retransform into the greenish substance; hence the two substances are mutually transformable, viz., one into the other by alkali and vice versa by acid :



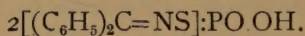
The authors have endeavoured to isolate thiobenzophenoxime, $(\text{C}_6\text{H}_5)_2:\text{C}=\text{NSH}$, from those two substances by different possible ways, but not succeeded. Now, they have to interpret the reactions regarding the formation of thiobenzanilide from benzophenoxime by the action of phosphorus pentasulphide as shown in the following scheme :



(4)



EXPERIMENTAL PART.

Thiobenzophenoxime Oxyphosphoryl Ester,

19 Grms. freshly prepared benzophenoxime dissolved in 600 c.c. of absolute ether was mixed with 4.4 grms. powdered phosphorus pentasulphide with the addition of 4.3 grms. phosphorus pentoxide, and the mixture was heated over a water bath with a reflux condenser for about six hours. Now the colourless ether was charged with greenish yellow colour; then the greater part of ether was removed by distillation, and its residual part driven off by passing a current of dry air through the solution, and finally sucked by pumping for removing the last trace of ether. By such a process of treatment there was left a greenish yellow substance of fibrous structure which is assumed to be thiobenzophenoxime oxyphosphoryl ester, and an intermediate product in the Beckmann rearrangement of the hypothetical thiobenzophenoxime. Its purification was exceedingly difficult on account of its excessive readiness of rearrangement.

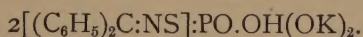
The determination of its molecular weight was, however, attempted with the crude substance by the cryoscopic method using benzene as solvent, expecting that its proximate value may be obtained so as to throw some light upon the nature of the substance :

	Grm. subst. taken	Lowering of the freez. point.		
I.	0.1151	0.085°		
II.	0.1846	0.132°		
Mol. weight calc. for		Observed values		
2[(C ₆ H ₅) ₂ C:NS]PO.OH		I	II	Mean
488.5		395.9	408.5	402.4

The substance suffers rearrangement with an explosive violence

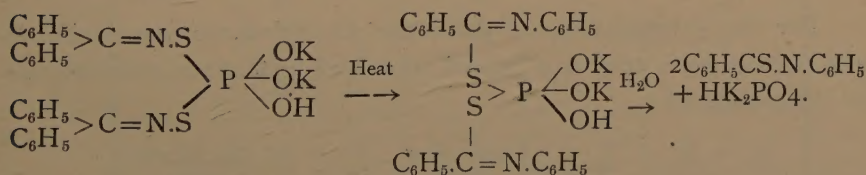
by mere heating to 70° , yielding a brownish yellow syrupy liquid with the evolution of a dense white fume. The syrup was dissolved in 10% aqueous solution of sodium hydroxide, and then by adding dilute hydrochloric acid the yellow precipitate produced. The latter was identified as thiobenzanilide by the melting point (98°) and other properties of the crystals deposited as thin plates from the alcoholic solution.

Thiobenzophenoxime Hydrodipotassium Orthophosphate,



By treating thiobenzophenoxime oxyphosphoryl ester with alcoholic potash at ordinary temperature, it has changed to a white crystalline powder. As the latter is almost insoluble in common organic solvents, its purification was exceedingly difficult; so the authors took the simple method of washing the substance with several different solvents such as alcohol, ether, petroleum ether, benzene, etc., which may dissolve the admixed impurities. So roughly purified substance was found to dissolve particularly in ethyl acetate and to crystallize in white transparent needles. The substance is sparingly soluble in cold water and behaves like soap forming froth by shaking; this may indicate that the substance would be an alkaline salt of a complex organic acid or soap, standing in harmony with the constitution of the substance above shown.

It also undergoes rearrangement with violence by heating up to 149° , producing thiobenzanilide and phosphoric acid by treating the product with water; the scheme of reaction may be assumed to be:



The substance was analysed and the following results were obtained.

For the determination of carbon and hydrogen, the substance was ignited with lead chromate.

	Grm. subst. taken	Grm. CO ₂ found	Grm. H ₂ O found
I.	0.1363	0.2704	0.0343
II.	0.2019	0.3919	0.0588
III.	0.1548	0.3047	0.0497

For the determination of nitrogen, the substance was also ignited with lead chromate.

	Grm. subst. taken	C.c. Nitrogen found	Temp. and press. observed
IV.	0.1325	5.72	20° and 758.1 m.m.
V.	0.2442	10.50	20° and 757.8 m.m.
VI.	0.2742	12.10	19.5° and 754.3 m.m.

For the determination of sulphur the substance was oxidized with fuming nitric acid (sp. gr. 1.5) in a sealed tube, and sulphur estimated as BaSO₄ as usual.

	Grm. subst. taken	BaSO ₄ found
VII.	0.2000	0.1718
VIII.	0.4246	0.3807
IX.	0.5834	0.5210

For the determination of phosphorus, the substance was similarly treated as in the case of sulphur, and phosphorus estimated as magnesium pyrophosphate:

	Grm. subst. taken	Mg ₂ P ₂ O ₇ , found
X.	0.2525	0.0530
XI.	0.2135	0.0399

For the determination of potassium the substance was oxidized with fuming nitric acid in a sealed tube, and potassium estimated as its chloroplatinate.

	Grm. subst. taken	Grm. K ₂ PtCl ₆ , found
XII.	0.3887	0.2986
XIII.	0.4097	0.3454

The percentage composition of the substance is given in the following table.

On the Solutions of Partial Differential Equations of the First Order at the Singular Points. II.

BY

Toshizô Matsumoto.

(Received June 30, 1919)

INTRODUCTION.

The homogeneous partial differential equation of the first order

$$Xf \equiv \xi_1(x) \frac{\partial f}{\partial x_1} + \xi_2(x) \frac{\partial f}{\partial x_2} + \dots + \xi_n(x) \frac{\partial f}{\partial x_n} = 0,$$

where $\xi_1(x), \xi_2(x), \dots, \xi_n(x)$ being holomorphic about the point $(0, 0, \dots, 0)$ and

$$\xi_i(x) = \lambda_i x_i + \dots, \quad i = 1, 2, \dots, n,$$

the dotted part being terms of higher degrees, has $n-1$ algebroidal solutions in the vicinity of the point $(0, 0, \dots, 0)$, provided $\lambda_1, \lambda_2, \dots, \lambda_n$ satisfy the following conditions:

I.° the relations

$$\lambda_1 p_1 + \lambda_2 p_2 + \dots + \lambda_i p_i + \dots + \lambda_n p_n = \lambda_i, \quad i = 1, 2, \dots, n$$

are not satisfied by any positive integral values of $p_1, p_2, \dots, p_n$, provided $p_1 + p_2 + \dots + p_n \geq 2$;

2.° if we denote $\lambda_1, \lambda_2, \dots, \lambda_n$ by the points on a plane, then we can trace a convex polygon in which these n points lie but which does not contain the origin; or we may say that this is a straight line through the origin, on one side of which all the n points lie.

In the previous memoir¹ these are called *Poincaré's conditions*;

¹ T. Matsumoto, Memoir of the College of Science, Kyoto Imp. Univ., Vol. II, No. 5 (1917), On the solutions...

and the writer discussed the case where the coefficients $\xi_1(x), \xi_2(x), \dots, \xi_n(x)$ commence by general linear homogeneous functions of $x_1, x_2, \dots, x_n$; and the case of a complete system. In both cases Poincaré's conditions had a determinative power for the existence of solutions, i.e., for the existence of holomorphic solutions of the equations: $Xf = \lambda_i f$, $i = 1, 2, \dots, n$. In the first part of the present memoir, the author wishes to make, about this equation, some comments with respect to Poincaré's conditions and in the next part some considerations of the equation $Xf = \lambda_i f$ are extended over the partial homogeneous differential equations of a higher order in which we shall obtain a glance at the relations existing between our problem and the ordinary differential equations of Fuchs' class.

I.

1. When the system of numbers $\lambda_1, \lambda_2, \dots, \lambda_n$ satisfy the second part of Poincaré's conditions but not the first part i.e., if for positive integral values of $p_1, p_2, \dots, p_n$ a relation e.g., for $i = n$:

$$p_1 \lambda_1 + p_2 \lambda_2 + \dots + p_n \lambda_n = \lambda_n, \quad (1)$$

exist, we shall prove that *the total number of such relations is finite*. For when such relations as (1) would exist for infinitely many times, then the total sum of integers: $p_1 + p_2 + \dots + p_n$ must increase indefinitely. But since $\lambda_1, \lambda_2, \dots, \lambda_n$ satisfy the second part of Poincaré's conditions, as usual the centre of masses

$$\frac{p_1 \lambda_1 + p_2 \lambda_2 + \dots + p_n \lambda_n}{p_1 + p_2 + \dots + p_n} \quad (2)$$

cannot be the origin, i.e., its absolute value must always be greater than a positive number ϵ . But when $p_1 + p_2 + \dots + p_n$ become sufficiently great, the ratio

$$\frac{p_1 \lambda_1 + p_2 \lambda_2 + \dots + p_n \lambda_n - \lambda_n}{p_1 + p_2 + \dots + p_n - 1}$$

approaches (2). Therefore from certain value of $p_1 + p_2 + \dots + p_n$, (1) can not be satisfied.

2. To test whether such a relation as (1) exist between λ 's, let g be a straight line on one side of which the n points $\lambda_1, \dots, \lambda_n$ lie.

Multiply these numbers by $e^{\alpha i}$, where α is a certain real quantity. Then all the real parts of $\lambda_1 e^{\alpha i}$, $\lambda_2 e^{\alpha i}$, ..., $\lambda_n e^{\alpha i}$ may be made positive; for the multiplication by such a number is nothing but a rotation of amount α , of the straight line g about the origin, and hence g may be made to coincide with the y -axis. Therefore assume the transformation has already been done, then the real parts of $\lambda_1, \lambda_2, \dots, \lambda_n$ are all positive. Moreover suppose that the real parts of

$$\lambda_1, \lambda_2, \dots, \lambda_n \quad (3)$$

are of an increasing order. Then if a relation hold:

$$p_1 \lambda_1 + p_2 \lambda_2 + \dots + p_i \lambda_i + \dots + p_n \lambda_n = \lambda_i,$$

then $p_1, \dots, p_n$ must be zero, or else after our arrangements, the real part of the sum of the terms of the left-hand side is greater than that of λ_i . This is absurd. Therefore it is only possible that

$$p_1 \lambda_1 + p_2 \lambda_2 + \dots + p_{i-1} \lambda_{i-1} = \lambda_i. \quad (4)$$

Therefore we may determine all possible relations such as (4).

3. Given the equation

$$Xf \equiv (\lambda_1 x_1 + \dots) \frac{\partial f}{\partial x_1} + (\lambda_2 x_2 + \dots) \frac{\partial f}{\partial x_2} + \dots + (\lambda_n x_n + \dots) \frac{\partial f}{\partial x_n} = \lambda_j f, \quad (5)$$

where the dotted parts stand for terms of higher degrees, suppose, $\lambda_1, \lambda_2, \dots, \lambda_n$ being in the previous arrangement (3), that

$$p_1 \lambda_1 + \dots + p_i \lambda_i = \lambda_j, \quad i < j, \quad (6)$$

where $p_1, \dots, p_i$ are positive integers whose total sum is not less than 2. We make a further assumption that in (6) none of $\lambda_1, \dots, \lambda_i$ can linearly be expressed by the other, i.e., they fulfil the first part of Poincaré's conditions. This assumption is possible, for if λ_i be not so, then we have only to eliminate it from (6). But as we have proved, since the total number of such a relation as (6) is finite, the case may occur where $p_1 + \dots + p_i$ is maximum. Under these conditions the equation (5) has a holomorphic solution commencing with the term

$$\begin{matrix} p_1 & p_i \\ x_1 & \dots x_i : \\ f_j = x_1^{p_1} & \dots x_i^{p_i} + \dots, \end{matrix} \quad (7)$$

By the method of calculations of limits, often used in the previous

Memoir, the *unique existence* of the solution f_j can easily be proved. It is our purpose to show that this solution is not helpful for solving $Xf=0$.

Since $\lambda_1, \dots, \lambda_i$ satisfy both parts of Poincaré's conditions, the equations

$$Xf = \lambda_h^* f, \quad h=1, \dots, i, \quad (8)$$

have holomorphic solutions of the form

$$f_h = x_h + \dots, \quad h=1, \dots, i,$$

the dotted parts being terms of higher degrees. Now consider the product

$$F \equiv f_1^{p_1} \dots f_i^{p_i} = x_1^{p_1} \dots x_i^{p_i} + \dots$$

Then clearly by (6),

$$XF = (p_1 \lambda_1 + \dots + p_i \lambda_i) F = \lambda_j F.$$

On the other hand since the solution f_j is unique, it must hold that

$$f_j \equiv F = f_1^{p_1} \dots f_i^{p_i}. \quad Q.E.D.$$

II.

1. Now consider the equation

$$\begin{aligned} & (ax^2 + \dots) \frac{\partial^2 f}{\partial x^2} + (2bxy + \dots) \frac{\partial^2 f}{\partial x \partial y} + (cy^2 + \dots) \frac{\partial^2 f}{\partial y^2} \\ & + (hx + \dots) \frac{\partial f}{\partial x} + (ky + \dots) \frac{\partial f}{\partial y} + (\lambda + \dots) f = 0, \end{aligned} \quad (1)$$

where a, b, c, h, k, λ are constants not zero and the dotted parts stand for terms of higher degrees written before. All the functions being holomorphic about $(0, 0)$, the origin $(0, 0)$ is a singular points of this equation.

At the origin, we must have

$$\lambda(f)_0 = 0, \quad \text{hence } (f)_0 = 0.$$

Differentiating (1) by x resp. y and putting $x=y=0$, we have

$$(h+\lambda) \left(\frac{\partial f}{\partial x} \right)_0 = 0, \quad (k+\lambda) \left(\frac{\partial f}{\partial y} \right)_0 = 0.$$

If neither $h+\lambda$, nor $k+\lambda$ be zero, we must take

$$\left(\frac{\partial f}{\partial x}\right)_0 = \left(\frac{\partial f}{\partial y}\right)_0 = 0.$$

Differentiating with respect to x twice, x and y , finally y twice, we have, for $(0, 0)$.

$$(2a + 2h + \lambda)\left(\frac{\partial^2 f}{\partial x^2}\right)_0 = 0,$$

$$(2b + h + k + \lambda)\left(\frac{\partial^2 f}{\partial x \partial y}\right)_0 = 0,$$

$$(2c + 2k + \lambda)\left(\frac{\partial^2 f}{\partial y^2}\right)_0 = 0,$$

Therefore suppose e.g., λ satisfy the equation

$$2a + 2h + \lambda = 0, \quad (2)$$

then the solution f of the equation (1) commences by x^2 .

2. Now differentiate the equation (1), p -times with respect to x and q -times with respect to y , then for $x=y=0$, the term with differential quotient of highest order is found to be

$$\begin{aligned} & \left[a \binom{p}{2} 2 + 2bpq + c \binom{q}{2} 2 + hp + kq + \lambda \right] \left(\frac{\partial^{p+q} f}{\partial x^p \partial y^q} \right)_0 \\ &= [ap^2 + 2bpq + cq^2 + (h-a)p + (k-b)q + \lambda] \left(\frac{\partial^{p+q} f}{\partial x^p \partial y^q} \right)_0, \end{aligned}$$

the other being of lower order. If the coefficient

$$ap^2 + 2bpq + cq^2 + (h-a)p + (k-b)q + \lambda \quad (3)$$

does not vanish for any positive integral values of p, q such as

$$p + q \geq 3, \quad (4)$$

then we may calculate all the values of differential quotients at $x=y=0$, step by step.

3. Now put

$$f \equiv Ax^2 + v, \quad (5)$$

A being a constant, the equation (1) may be written as follows:

$$\begin{aligned} & ax^2 \frac{\partial^2 v}{\partial x^2} + 2bxy \frac{\partial^2 v}{\partial x \partial y} + cy^2 \frac{\partial^2 v}{\partial y^2} + hx \frac{\partial v}{\partial x} + ky \frac{\partial v}{\partial y} + \lambda v \\ &= \varphi_{20} \frac{\partial^2 v}{\partial x^2} + \varphi_{11} \frac{\partial^2 v}{\partial x \partial y} + \varphi_{02} \frac{\partial^2 v}{\partial y^2} + \psi_1 \frac{\partial v}{\partial x} + \psi_2 \frac{\partial v}{\partial y} + \theta v + \chi, \end{aligned} \quad (6)$$

where φ_{20} , φ_{11} , φ_{02} , χ commence at least by terms of the third degree, ψ_1 , ψ_2 by the second degree, θ by the first degree. Let M be the maximum modulus of these functions, r the smallest radius of convergent circles about (o, o) , then we have, as fonctions majorantes,

$$\begin{aligned} |\varphi_{20}|, |\varphi_{11}| &\leq \frac{M\left(\frac{x+y}{r}\right)^3}{1 - \frac{x+y}{r}} \\ |\varphi_{02}|, |\chi| &\leq \frac{M\left(\frac{x+y}{r}\right)^2}{1 - \frac{x+y}{r}}, \\ |\psi_1|, |\psi_2| &\leq \frac{M\left(\frac{x+y}{r}\right)}{1 - \frac{x+y}{r}}, \\ |\theta| &\leq \frac{M\left(\frac{x+y}{r}\right)}{1 - \frac{x+y}{r}}. \end{aligned}$$

Hence consider the equation

$$\begin{aligned} &\varepsilon \left(x^2 \frac{\partial^3 V}{\partial x^2} + 2xy \frac{\partial^2 V}{\partial x \partial y} + y^2 \frac{\partial^2 V}{\partial y^2} + x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} - V \right) \\ &= \frac{M\left(\frac{x+y}{r}\right)^3}{1 - \frac{x+y}{r}} \left(\frac{\partial^3 V}{\partial x^3} + \frac{\partial^3 V}{\partial x \partial y} + \frac{\partial^3 V}{\partial y^2} + 1 \right) \\ &+ \frac{M\left(\frac{x+y}{r}\right)^2}{1 - \frac{x+y}{r}} \left(\frac{\partial V}{\partial x} + \frac{\partial V}{\partial y} \right) + \frac{M\left(\frac{x+y}{r}\right)}{1 - \frac{x+y}{r}} V, \end{aligned} \quad (7)$$

where ε is to be determined. Every term of each coefficient of the right-hand side of (6) is, in absolute value, less than the corresponding term of (7). Now differentiating the equation (7) p -times with respect to x and q -times with respect to y and put $x=y=o$, we get, from the left-hand side of (7), the differential quotient of highest order,

$$\varepsilon (p^2 + 2pq + q^2 - 1) \left(\frac{\partial^{p+q} V}{\partial x^p \partial y^q} \right)_o.$$

Therefore if for $p+q \geq 3$,

$$\frac{|ap^2 + 2bpq + cq^2 + (h-a)p + (h-b)q + \lambda|}{(p+q)^2 - 1} \geq \varepsilon > 0, \quad (8)$$

the series calculated from (7) serves for *fonction majorante* of that of (6).

4. The fraction (8), for sufficiently great $p+q$, is nearly equal to

$$\frac{|ap^2 + 2bpq + cq|}{(p+q)^2}, \quad (9)$$

There if 1^0 , the sum (3), *i.e.*, numerator of (8) do not vanish for $p+q \geq 3$, and 2^0 , the points a, b, c marked on Gauss' plane lie all on one side of a straight line through the origin, the inequality (8) may be fulfilled. These are nothing but Poincaré's conditions.

Under these conditions we shall prove the existence of a power-series commencing with terms of the third degree in x and y which satisfy the equation (7). Put

$$x+y \equiv u,$$

then we see, in the equation (7), that V is a function of u and it may be written as follows:

$$\begin{aligned} & \varepsilon \left(u^2 \frac{d^2 V}{du^2} + u \frac{dV}{du} - V \right) \\ &= \frac{M}{r^2} \frac{u^3}{r-u} \left(3 \frac{d^2 V}{du^2} + 1 \right) + \frac{M}{r} \frac{u^2}{r-u} \left(2 \frac{dV}{du} \right) + M \frac{u}{r-u} V. \end{aligned} \quad (10)$$

This equation, after dividing by ε , may be written in the following form:

$$u^2(1+\dots) \frac{d^2 V}{du^2} + u(1+\dots) \frac{dV}{du} - (1+\dots)V = mu^4 + \dots, \quad (11)$$

the dotted parts stand for the terms of higher degrees written before and m is a constant.

To solve this equation (11), consider the equation without the second member:

$$u^2(1+\dots) \frac{d^2 V}{du^2} + u(1+\dots) \frac{dV}{du} - (1+\dots)V = 0. \quad (12)$$

This equation belongs to the equations of the second order of Fuchs' class. Its characteristic equation is

$$\varphi(r) \equiv r(r-1) + r - 1 = 0.$$

The roots of this equation at $u=0$ are

$$r_1 = 1, \quad r_2 = -1,$$

where $r_2 - r_1 = -2$ which is not a positive integer. Therefore the equation (12) has an integral

$$V_1 = u U(u), \quad (13)$$

where $U(u)$ is holomorphic and $U(0) \neq 0$. To find the integral of (11), put

$$V = C \cdot V_1 = CuU(u),$$

where the function C is to be determined.

Putting

$$\frac{dC}{du} \equiv z,$$

z is found to satisfy the equation

$$u(U(0) + \dots) \frac{dz}{du} + (3U(0) + \dots)z = mu + \dots$$

Therefore z is of the form

$$z = \frac{m}{4U(0)} u(1 + \dots).$$

Hence

$$C = \int z du = \frac{m}{8U(0)} u^2(1 + \dots),$$

V = power-series commencing by the term u^3 .

Thus our equation (7) has holomorphic solution commencing by $(x+y)^3$, which is the required *fonction majorante* of the solution $v(x, y)$ of the equation (6). Hence, the partial differential equation (1) :

$$\begin{aligned} & (ax^2 + \dots) \frac{\partial^2 f}{\partial x^2} + (2bxy + \dots) \frac{\partial^2 f}{\partial x \partial y} + (cy^2 + \dots) \frac{\partial^2 f}{\partial y^2} \\ & + (hx + \dots) \frac{\partial f}{\partial x} + (ky + \dots) \frac{\partial f}{\partial y} + (\lambda + \dots)f = 0, \end{aligned}$$

where the dotted parts mean terms of higher degrees than the foregoing terms, under Poincaré's conditions has a holomorphic solution of the form

$$f = Ax^3 + \dots,$$

provided the equation (2) be fulfilled:

$$2a + 2h + \lambda = 0.$$

5. The result can easily be extended to the case where the first part of Poincaré's conditions is not satisfied, namely when

$$ap^2 + 2bpq + cq^2 + (h-a)p + (k-b)q + \lambda = 0. \quad (3')$$

Suppose this relation is the last one where $p+q$ is a maximum integer. Then

$$\left(\frac{\partial^{p+q} f}{\partial x^p \partial y^q} \right)_0$$

is arbitrary. Hence put, instead of (5),

$$f \equiv Ax^p y^q + v,$$

then in (6) the function χ will commence with terms of $(p+q+1)$ *th* degree, the other remaining the same. Consequently the second member of (11) will be of the form

$$mu^{p+q+1} + \dots$$

Moreover C will commence with u^{p+q} . Therefore the lowest power in V is $p+q+1$, hence v will commence by the power $p+q+1$. Thus, when a, b, c lie on one side of a straight line through the origin, our equation (1) has still a holomorphic solution in the vicinity of $(0, 0)$.

6. Our considerations may be extended easily for cases of equations of higher order or for cases of equations depending upon variables more than two. For the equation of higher order a little modification is necessary. Let us consider the equation of the n th order with two variables:

$$\begin{aligned} & (a_{n,0}x^n + \dots) \frac{\partial^n f}{\partial x^n} + \left(\binom{n}{1} a_{n-1,1} x^{n-1} y + \dots \right) \frac{\partial^n f}{\partial x^{n-1} \partial y} + \dots + (a_{0,n} y^n + \dots) \frac{\partial^n f}{\partial y^n} \\ & + (\delta_{n-1,0} x^{n-1} + \dots) \frac{\partial^{n-1} f}{\partial x^{n-1}} + \left(\binom{n-1}{1} \delta_{n-2,1} x^{n-2} y + \dots \right) \frac{\partial^{n-1} f}{\partial x^{n-2} \partial y} \dots \\ & + (\delta_{0,n-1} y^{n-1} + \dots) \frac{\partial^{n-1} f}{\partial y^{n-1}} \\ & + \dots \dots \dots \\ & + (h_{1,0} x + \dots) \frac{\partial f}{\partial y} + (h_{0,1} y + \dots) \frac{\partial f}{\partial y} + \lambda f = 0 \end{aligned} \quad (14)$$

where in general the term of lowest degree in the coefficient of

$\frac{\partial^m f}{\partial x^{m-l} \partial y^l}$ is $\binom{m}{l} x^{m-l} y^l$ multiplied by a constant.

For this equation, the equation corresponding to (11) is of the form:

$$u^n(1+\dots)\frac{d^n V}{du^n} + u^{n-1}(1+\dots)\frac{d^{n-1} V}{du^{n-1}} + \dots + u(1+\dots)\frac{dV}{du} - (1+\dots)V = mu^h, \quad (15)$$

the dotted part being as usual terms of higher degrees. The characteristic equation of (15) without the second member is

$$\varphi(r) \equiv r(r-1)(r-2)\dots(r-n+1) + \dots + r(r-1) + r - 1 = 0. \quad (16)$$

This equation has a root $r_1 = 1$, and the other roots cannot be a positive integer greater than unity. Therefore when r_i runs the series of the other roots, $r_i - r_1$ cannot be a positive integer. Hence our Fuchs' equation, the equation (15) without the second member, has a holomorphic integral commencing with the term u , while the other integral cannot be holomorphic at $u=0$.

7. To prove the existence of a holomorphic solution of the equation (15), consider in general the equation

$$F(V) \equiv p_0 \frac{d^n V}{du^n} + p_1 \frac{d^{n-1} V}{du^{n-1}} + \dots + p_i \frac{d^{n-i} V}{du^{n-i}} + \dots + p_{n-1} \frac{dV}{du} + p_n V = p.$$

Then

$$\begin{aligned} p \frac{dF}{du} - F \frac{dp}{du} &= p p_0 \frac{d^{n+1} V}{du^{n+1}} + (p p_0' + p p_1 - p' p_0) \frac{d^n V}{du^n} + \dots \\ &+ (p p_i' + p p_{i+1} - p' p_i) \frac{d^{n-i} V}{du^{n-i}} + \dots + (p p_{n-1}' + p p_n - p' p_{n-1}) \frac{dV}{du} \\ &+ (p p_n' - p' p_n) V = 0. \end{aligned}$$

In our case

$$\begin{aligned} p_i &= u^{n-i} + \dots, \quad i=0, 1, \dots, n-1, \\ p_n &= -1 + \dots, \\ p &= mu^h + \dots, \\ p' &= mhu^{h-1} + \dots, \\ p p_i' + p p_{i+1} - p' p_i &= (mu^h + \dots) ((n-i)u^{n-i-1} + \dots) + (mu^h + \dots) (u^{n-i-1} + \dots) \\ &\quad - (mhu^{h-1} + \dots) (u^{n-i} + \dots) \\ &= mu^{h-1} (n+1-i-h)u^{n-i} + \dots, \\ p p_0' + p p_1 - p' p_0 &= mu^{h-1} (u^{n+1} + \dots), \\ p p_{n-1}' + p p_n - p' p_{n-1} &= mu^{h-1} (-hu + \dots), \\ p p_n' - p' p_n &= mu^{h-1} (h + \dots). \end{aligned}$$

Hence the equation

$$p \frac{dF}{du} - F \frac{dp}{du} = 0, \quad (17)$$

will be, after dividing by mu^{h-1} ,

$$\begin{aligned} & (u^{n+1} + \dots) \frac{d^{n+1}V}{du^{n+1}} + ((n+1-h)u^n + \dots) \frac{d^n V}{du^n} + \dots \\ & + ((n+1-i-h)u^{n-i} + \dots) \frac{d^{n-i} V}{du^{n-i}} + \dots \\ & + (-hu + \dots) \frac{dV}{du} + (h + \dots)V = 0. \end{aligned} \quad (18)$$

The characteristic equation is, therefore,

$$\begin{aligned} \varphi(r) & \equiv r(r-1)(r-2)\dots(r-n) + (n+1-h)r(r-1)(r-2)\dots(r-n+1) + \dots \\ & + (n+1-i-h)r(r-1)(r-2)\dots(r-n+i+1) + \dots + (-h)r + h = 0. \end{aligned}$$

But since

$$\begin{aligned} & h(h-1)\dots(h-n+i) + (n+1-i-h)h(h-1)\dots(h-n+i+1) \\ & = h(h-1)\dots(h-n+i+1), \end{aligned}$$

we have by successive calculation

$$\varphi(h) = h(h-1) - h^2 + h = 0.$$

Thus h is a root of the characteristic equation $\varphi(r) = 0$. Moreover if this equation has an integral root, then it must be a divisor of h ; therefore when r_i runs the series of the other root, $r_i - h$ cannot be a positive integer. Therefore the equation (18) has a holomorphic integral such as

$$V = Ku^h + \dots,$$

K being a constant. As we have said in the preceding paragraph, this cannot be an integral of the equation (15) without the second member. Hence from (17),

$$F(V) = c p,$$

c being a constant. Therefore $\frac{V}{c}$ is an integral of the equation (15). Thus our equation (15) has a holomorphic solution commencing with u^h which serves as the *fonction majorante* of the equation (14). Thus we may conclude as follows: *The equation (14), has always a holomorphic solution in the vicinity of (0, 0) provided $a_{n,0} \dots a_{0,n}$ marked as points of a Gauss' plane, lie on one side of a straight line through the origin.* It is of-course necessary that λ satisfy such an equation as (3').



Brush and Glow Discharges of Electricity and the Formation of Spark.

BY

Usaburo Yoshida and Hideki Hirata.

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I. Brush Discharges.

In the previous investigations¹ carried out by one of the writers on the figures produced on photographic plates by electric discharges, regular cathode—and irregular anode—figures were observed. A photographic plate was laid on a sheet of tin foil, and when the two electrodes placed on the plate were placed in contact momentarily with the cathode and the anode of an influence machine respectively, fine images of brush discharges were impressed on the plate. The cathode figure consisted of regular branches which radiated outward from the cathode and terminated rather regularly. On the other hand, the anode figure consisted of many branches which radiated also outward from the anode, each branch changing its path irregularly and have divided into further branchlets in an irregular manner, and these branchlets terminated also irregularly in sharp points. It was also noted that an anode branch consisted of two parts, namely a more intense portion near the electrode and a weaker portion farther away.

When one of the electrodes on the photographic plate was connected by means of a conductor with the tin foil under the plate, a brush discharge was produced only at the other electrode, which was not connected with the foil. When this latter electrode was anode, an anode figure was obtained at this electrode. Experimenting under such conditions, it was observed that the spark did not yet pass between the electrodes, though the ends of the weaker parts of some

¹ U. Yoshida, Mem. Coll. Sci. Kyoto, 2, p 105, and 315, (1917).

anode branches reached the cathode. A spark discharge seemed then to pass between the electrodes, only when an intense portion of an anode branch reached the cathode which was connected with the tin foil under the photographic plate.

In a cathode branch, no such two portions of different natures as those in an anode branch were detected. And a spark discharge seemed always to pass between the electrodes when the end of a cathode branch reached the anode which was connected with the tin foil under the plate.

Let us now consider the brush discharges which take place in the air at atmospheric pressure. The cathode and the anode brush discharges appear at each electrode of an influence machine separately if the distance between them is properly increased and the electric capacity between them is not large.

The appearances of the brushes thus obtained are different in positive and negative discharges. According to K. Wesendonck¹ the appearance of a positive brush was very similar to that of a tree; beginning from its start at the anode, it was divided into several branches which were also subdivided into many weak branchlets. As to a negative brush he also noted that it did not show any branching with a spherical cathode of not a large diameter.

In the present experiment a two-plates-influence-machine of Wehrsen type was used. When the two metallic spherical electrodes of one or two centimetre in diameter were separated to a proper distance, and when the electric capacity between them was made small, positive and negative brushes might be made visible at each electrode separately with a non-luminous region between them. Under such experimental conditions, negative brushes of a reddish purple colour issued from the cathode at that portion of its surface, in most cases, just opposite the anode, and approaching more toward the anode they become diffused more and more and at last terminated in a diffuse boundary. They never showed any regular branching as in the case of a cathode figure on a photographic plate, or any irregular branching as in a positive brush. On the other hand the positive brushes issued from the anode at the portion of its surface just opposite the cathode and showed their characteristic irregular branchings as noted by K. Wesendonck. It was especially noticeable that a positive brush consisted of two parts, namely a more intense part of reddish purple tint

¹ K. Wesendonck, *Ann. d. Phys. u. Chem.*, **30**, p. 1, (1887).

nearer to the anode and a weaker part of bluish purple colour farther away as was observed in an anode-discharge-figure on a photographic plate.

Now, one of the two spherical electrodes before mentioned was replaced by a plane electrode of about 10 cm. in diameter and about 1.5 cm. in thickness, which had a smooth edge. The capacity between the electrodes was made small, so that it was more favorable for brush than for spark discharge to take place. Under such experimental conditions brush discharges took place only at the other spherical electrode, and no kind of visible discharge was detected at the plane electrode. When the two electrodes were held at a sufficient distance apart, positive brushes which issued from the spherical anode did not reach the plane cathode, and no luminosity was detected in the region extending from the ends of the positive brushes to the surface of the cathode. Decreasing the distance between the electrodes, gradually a state was reached such that though many fine branches of weak intensities of positive brushes reached the plane cathode yet no spark passed between the electrodes. By yet approaching the electrodes, another state of discharge is reached such that sometimes a spark passed between the electrodes, and sometimes many brush discharges appeared also successively from the anode. In this state of discharge many intense branches of positive brushes extended to the region adjacent to the front surface of the plane cathode, but it was never observed that these intense branches extended to the cathode itself without causing a spark to pass along any one of their paths. This difference of nature between the weaker part and the stronger one of the positive brush is quite similar to that observed in the case of a positive brush on a photographic plate.

Next, reversing the signs of the poles, a similar observation on negative brushes from the spherical cathode was made. In this case the boundary of the end of a negative brush was not well defined as was stated before, and it was not possible, of course, to speak about its end definitely. But the observation showed that a spark seemed then to pass between the electrodes, only when a weak diffuse luminosity at the end of a negative brush occupied the whole space up to the plane anode. This nature of negative brushes is similar to that of a cathode branch on a photographic plate.

In the case of the discharge figures on the photographic plate, an explanation of their formation based on the consideration of ioni-

sation by collisions of positive ions and electrons with gas molecules was given by one of the writers. In that case the condition that the ions on the photographic plate were attracted by the tin foil under the plate was, of course, taken into account; and especially the formation of the fine regular cathode branches was considered to be due to that condition. In the case of brush discharges in the air at atmospheric pressure this condition is absent. But essentially the same consideration as before seems to be applicable in explaining the main features of positive and negative brushes in this case.

Now a gas will be ionised by collisions of positive and negative ions and electrons with the molecules of the gas. Among these the electrons will be more efficient ionisers than the others which have a greater mass; and the luminosity at the ends of positive and negative brushes will be due to the ionisation by collisions of electrons with the molecules of the air.

The electrons at the end of a negative brush will be supplied by the ionisation by collisions of positive ions with cathode or air molecules near the cathode, and also by the ionisation by collisions of electrons with the air molecules in the region between the cathode and the end of the brush. The electrons at the end of a negative brush thus formed will be repelled by the cathode, and at the same time the positive ions will be attracted toward it. Consequently at the end of a negative brush a great number of electrons will be in excess, and the potential gradient in front of the negative brush will become so large that the molecules of the air are ionised by the collisions of these electrons. The prolongation of a negative brush will occur in such a manner. As the electrons at the end of a negative brush are many in number they will repel each other with considerable force. This combined with the rapid mobility of electrons seems to be the cause of the fact that the end of a negative brush is diffused in its boundary.

Next, in front of the anode, the electrons will be attracted toward it. When the strength of the electric field attains a certain value, they will ionise the air molecules in their journey to the anode, and many positive and negative ions and electrons will be formed. The electrons thus set free will also be attracted toward the anode, and ionise the air by their collisions with its molecules. The positive ions thus formed and left behind will not diffuse immediately, and will retain their positions for a short time owing to their slow mobility.

Consequently in the neighbourhood of a positive brush thus formed, wherein a great number of positive ions is present, the intensity of the electric field may become very strong. If some electrons, which come from the cathode or elsewhere, should happen to be in such field they will also ionise the gas by their collisions with its molecules in their journey to the anode branch mentioned above. And by the same process as described above, the prolongation of an anode brush will take place. Considering in this manner, the peculiar nature of a positive brush, that it has many fine irregular branches toward the cathode seems to be easily understood; because the formation of these branches is primarily due to the presence of electrons which would initially be few in number and distributed rather irregularly.

Next, the well known fact that the positive brush is longer than the diffuse negative brush may be explained in the following manner. At the end of a fine positive brush the positive ions, and at the end of a diffuse negative brush the electrons are in excess respectively. Among these the electrons, owing to their rapid mobility, will diffuse more readily by their mutual repulsions, and the density of the negative charge at the end of a negative brush will be liable to become rare. This will have the effect that a stronger electric field may be established more easily in the neighbourhood of the end of an anode branch. And this is more favorable for the positive brush in its prolongation than for the negative.

It is already mentioned that there are two parts of different natures in a positive brush: one of stronger intensity and the other of weaker intensity further away from the anode. Among these the stronger branch is always accompanied by a weaker branch as its continuation at the end. This fact is also observable clearly in the case of brush discharge on a photographic plate. Moreover, when the potential difference between the electrodes is moderately decreased, the stronger positive brushes disappear entirely, and the brushes of weaker intensity alone are visible at the anode. Judging from these facts it seems natural to consider that the weaker brush appeared previously at the anode and then the brush of stronger intensity is formed along the path made by the former.

In the case of brush discharges on a photographic plate it was assumed that the weaker part of a positive brush was the path of the ionisation by collisions of electrons with the molecules of the air, and that the ionisation by collisions of positive ions with air molecules oc-

curred in the branches of stronger intensity. When once a branch of the positive brush of weaker intensity is formed momentarily by the ionisation by collisions of electrons with the molecules of the air, the electrons and the negative ions thus formed are attracted toward the anode, and the positive ions are left behind. Though the air in that branch will be in a condition, by the previous ionisation, that it might be more easily ionised by the collisions of electrons with its molecules, yet the intensity of the electric field in that branch will be so much reduced by such distribution of ions that it is insufficient to cause the ionisation by collisions of electrons with air molecules in it.

When the potential of the anode is gradually raised, the positive brush of weaker intensity grows more, and its length and the number of branches are increased. In this state of its growth, many negative ions and electrons produced at the end of each branch of the brush are attracted and move toward the anode. And in their journey to the anode most of them will move along the paths made by the previous ionisation by collisions of electrons with air molecules, that is along the branches of the weaker brush, because the potentials in every branches are higher than those in their immediate neighbourhood due to the presence of the excess of positive ions in every parts of the branches. Consequently the gas in the branches will be more easily ionisable by the collisions of electrons and of positive ions with its molecules at least due to the increase of their temperatures by the rapid movements of electrons along them. Moreover the electric force in a branch in the immediate neighbourhood of the anode will be tolerably increased by the accumulation of negative ions and electrons toward the anode, and the gas in this strong electric field will be ionised by the collisions of positive ions and electrons with its molecules. And ionisation which occurs in this place will be more vigorous than those at the ends of the weaker positive brush before mentioned, because the gas in this place is in a more easily ionisable state and the number of electrons which ionise the gas in this place will be larger than those at the former. The negative ions and electrons produced at the ends of the weaker brush, are attracted toward the anode along the branches of the weaker brush; and by the accumulation of many of these negatively charged particles a strong electric field will be established in the place just in front of the group of a large number of positive ions formed by the previous intense ionisation. By the ionisation by collision of positive and negative ions and electrons

with the gas molecules in this place, a large number of electrons and positive ions will also be produced. The electrons and the negative ions being attracted toward the anode, the group of a large number of positive ions thus produced will be pushed away; and the same process being repeated as before the ionisation by collisions of positive and negative ions and electrons above noted will take place successively along the branches of the weaker positive brush. This process of comparatively vigorous ionisation will be accompanied by the emission of light of stronger intensity, and the fact that the stronger part of the positive brush follows along the paths of the weaker ones seems to be explained in such way.

In the case of a positive brush on a photographic plate, some cases were observed where a stronger branch of the positive branch made way, in some part of its path, across the neighbouring weaker branches. This will perhaps occur also in our case, and the irregularity of the path of the stronger branch will be increased by this condition.

When once a stronger branch of the positive brush is formed, the gas in this branch will be in an easily ionisable state, at least, due to the increase of its temperature. And the process of ionisation by collisions, at least of electrons with its molecules, will last for a short time after the formation of the stronger branch so far as the potential of the anode does not fall below a certain value.

Thus assuming the nature of the stronger branch of a positive brush the fact that the spark discharge is caused by the arrival of this branch to the cathode seems to be explained easily. In a weaker branch of a positive brush, the process of ionisation by collisions of electrons with the molecules of the air takes place only momentarily at the instant of its formation, and no more after its formation as was considered before. Moreover, the ionisation by collisions of positive ions with the molecules of the air does not occur in that part. If the weaker branch of a positive brush is of such a nature, the mere arrival of it at the cathode will not cause the spark discharge to pass between the electrodes as was observed in the present experiment and also in the case of a brush discharge on a photographic plate.

When a metal, with a comparatively large curvature such as a thin wire, was used as the cathode, a few short negative brushes were seen to issue from its surface. As these brushes glowed steadily, the process of the ionisation by collisions of electrons with the molecules of the air would be taking place simultaneously in all portions of these

brushes in contrary to the case of the weaker positive brushes where the ionisation by collisions of electrons was supposed to occur in a rather pulsatory manner at the moment of their formations. When a spherical cathode of larger diameter than a centimetre was used under the present experimental conditions, the negative brushes were never steady, but the fact that the spark discharge was caused by the arrival of the end of a negative brush to the plane anode seems to suggest that the ionisation by collisions of electrons is taking place simultaneously in every portion of this brush.

II. *Glow Discharge.*

When the spherical electrodes of one or two centimetres in diameter are separated at a proper distance, the capacity between them being reduced, positive and negative brush discharges are visible at each electrode respectively. Next, when the distance between the two electrodes is further increased, one may observe that an entirely different phenomenon of discharge takes place at the anode. The positive brush disappears entirely and the surface of the anode which is just opposite to the cathode is now covered with the thin film of a pale violet glow. This Phenomenon is called the positive glow discharge.

In regard to the question, in what circumstances the glow discharge takes place, many investigations have been made. But, so far as the writers are aware, this question is not definitely answered, and its nature remains still unexplained.

According to K. Wesendonck¹ the positive brush was easily converted to a glow discharge by the effect of blowing the air against the former. The writers repeated this experiment and observed that this effect was especially noticeable when the air was blown by a bellows.

As this effect of blowing the air against the brush seemed to the writers to be due to a rapid diffusion of great numbers of positive and negative ions and electrons in the brush, the opinion was immediately entertained that a uniform supply of a great many electrons toward the anode might be favorable to the phenomenon of the glow discharge.

By using a plane cathode and a spherical anode of one or two centimetres in diameter as the electrodes of an influence machine, and by reducing the capacity between the electrodes, only the positive brush discharge was made visible at the spherical anode by properly

¹ K. Wesendonck, *Wied. Ann.*, **40**, p. 481, (1890).

adjusting the distance between the electrodes. Next, when the air in the region between the electrodes was ionised by the passage of β and γ rays from radium bromide, the positive brushes disappeared instantaneously, and the surface of the spherical anode which was just opposite to the cathode was now covered with the thin film of a glow discharge. When the sample of radium bromide was taken away the brush discharge reappeared instantaneously, and the glow disappeared at that very moment. This was just as was expected. The same phenomenon was observed also with a spherical cathode, but with a little more difficulty, because the negative brush which issued from the spherical cathode called forth a dense accumulation of negative ions and electrons toward the narrow central portion of the surface of the anode which is just opposite to the cathode. It was already stated before that the phenomenon of glow discharge was easily observed at the spherical anode when the spherical cathode was separated at a comparatively long distance from the anode. In this case, negative ions and electrons from the negative brush would have to diffuse themselves in a wider area, and their distribution in front of the anode would be rather uniform.

When an infinite number of electrons of uniform distribution were present in front of the anode, the positive brushes, if once formed at the surface of the anode, would be enormous in number; and consequently the electric fields at their ends would not be so strong as in the other case where they were few in number. This circumstance would be unfavorable to the prolongation and consequently to the formation of the brushes. And the process of the ionisation by collisions of electrons with the air molecules would be confined to the region just in front of the anode, as was observed in the case of the anode glow discharge.

In order to illustrate the fact that the uniform supply of electrons to the anode is favorable to the formation of the anode glow, the photograph Fig. 1 is presented. In this case, two wires of about one millimeter in diameter were stretched, about four centimetres apart, parallel to one another, and served as the cathode and the anode of the influence machine respectively. At the beginning of the discharge the negative brushes, which were very short in this case and appeared like luminous points, flickered here and there on the surface of the cathode wire, and the anode glows also changed their places on the surface of the anode wire simultaneously. But after a short while, these short negative brushes became steady, and the anode glows

appeared also steadily on the surface of the anode wire just opposite to the negative brushes. In Fig. 1, the three separate luminous points are the images of three such steady negative brushes, and the three luminous threads, which occupy the positions just opposite to the former three are the images of the corresponding anode glows. The length of a luminous thread of the anode glow depends upon the distance between the two wires, the former increasing with the latter.

As no luminous discharge takes place at any portion of the anode surface where no such glow discharges are detected, we may infer that the electric field in this portion is not so strong as to cause the ionisation by collisions of electrons with the air molecules; and that in the other portion of the anode surface where the glow is visible it is strengthened by the accumulation of negative ions and electrons toward the anode.

If the uniform supply of a great number of electrons to the anode is favorable to the formation of the anode glow discharge as was considered before, any other condition, on the contrary, which is injurious to the uniform distribution of ions and electrons will be more favorable for the formation of the positive brush than for that of the anode glow. According to Wesendonck¹, an anode glow discharge was easily converted to a positive brush one by spreading metal powders on the surface of the anode or in the region between the electrodes.

In the preceding paragraph we have stated that the glow discharge took place at the anode when a great number of electrons of uniform distribution was supplied to the anode. But this is never always the case. By using a plane cathode and a spherical anode as was stated before and reducing the capacity between them, the distance between them and the rotation of the influence machine were so adjusted that, when the air in the region between them was ionised by the passage of β and γ rays from a sample of radium bromide, the discharge at the anode occurred in the form of a glow. Next, when the intensity of the electric field in front of the anode was increased to a certain amount by increasing the speed of rotation of the influence machine or by decreasing the distance between the electrodes, a reddish purple "luminous point" appeared in the pale violet luminous film of the glow on the surface of the spherical anode just opposite to the plane cathode where the electric field was strongest. In this state of discharge a few positive brushes also sometimes ap-

¹ K. Wesendonck, l.c.

peared at the anode. And it is especially noticeable that these positive brushes started always from the "luminous points" mentioned above. This was already observed by K. Wesendonk¹ and he called this "luminous point" "der Zündstoff eines Funkens." When the capacity between the electrodes was increased, the positive brushes which had started from the luminous points of the anode glow were converted to the spark discharges as was noted by Villard and Abraham.²

Here it must be remarked that the positive brush which started from a luminous point of the anode glow was always the stronger part of the positive brush before mentioned. A luminous point of the anode glow, thus being the starting point of a stronger positive brush, seems to be of the same nature as the latter. If the intensity of the electric field at a point on the front surface of the anode, where the glow discharge is taking place, is increased to a certain value, the positive ions in the glow will ionise the air at that point by their collisions; and much denser positive ions will be set free at this point than at the other portion of the glow. As these dense positive ions thus set free at this point are pushed ahead, they are in the same state as those at the end of a positive brush; and a positive brush will start from this point just as in the case of the prolongation of a positive brush.

M. Toepler³ investigated the glow and the brush discharge, etc., quantitatively. Taking the distance between the electrodes and the current as the abscissa and the ordinate respectively, he determined the domain of existence for each kind of discharge. According to him the positive brush assumed the domain of a stronger current than that of the anode glow. The writers are of opinion that the difference of current intensity is rather a consequence of the difference between the natures of the glow and the brush discharge and not the direct cause of the formation of either of them.

III. Spark Discharges.

B. Walter⁴ investigated the mechanism of the formation of a spark due to an induction coil by using the method of a moving photogra-

¹ K. Wesendonk, Verh. d. D. Phys. Ges., p. 514 (1912).

² Villard and Abraham, l.c.

³ Toepler, Ann. d. Phys., 2, p. 560, (1900).

⁴ B. Walter, Ann. d. Phys., 66, p. 636, (1898); and 68, p. 776, (1899).

phic plate, and observed that a spark discharge had passed between the electrodes along the path formed by preliminary positive and negative brushes. When a plane and a sphere were employed as the cathode and the anode of an influence machine respectively, the brush discharge appeared only at the spherical anode. By reducing the capacity and the distance between them properly a state was reached such that, in most cases, the discharge occurred in the form of a positive brush at the spherical anode, and sometimes in the form of a spark. Under such experimental conditions, the writers observed that the spark passed then between the electrodes when the end of a stronger positive brush reached the plane cathode. When the signs of the electrodes were interchanged, only negative brushes appeared at the spherical cathode, and under similar experimental conditions as before it was observed that the arrival of the end of a negative brush at the plane anode caused a spark discharge between the electrodes. These facts were already described in a former section. Next when two spheres of one or two centimetres in diameter were used as the cathode and the anode of the influence machine, the positive and the negative brushes were formed at each electrode respectively. Experimenting under a similar condition as before, it was observed that probably a spark passed then between the electrodes when the end of the stronger part of a positive brush had arrived at the end of a negative brush.

Next maintaining the other conditions unaltered, the capacity between the electrodes was increased a little in each of the three cases above mentioned, then the positive and the negative brushes were increased more in length but were reduced in number, that is the time-interval between the two successive brushes was increased. And consequently the spark discharges occurred more frequently than before. When the capacity between the electrodes was still further increased this tendency became more prominent and at last a state was reached when the discharge took place only in the form of sparks, and never in that of brushes. In the case of positive brushes and sparks which occurred in the state of glow discharge at the spherical anode, the same effect of capacity on the manner of discharge was also observed. The fact observed by Toepler¹ that the domain of existence of the spark discharge in his current—spark length—diagram increased contrariwise to those of brush and glow

¹ M. Toepler, *l.c.*

with the capacity, amounts to nothing more than has been stated before. When the capacity between the electrodes was increased, the decrement of the potential difference between the electrodes by the formation of a brush would be smaller, and the brush thus formed would become longer than before. By yet more increasing the capacity, the brush would become still longer. And at last when it was increased sufficiently, all of the brushes would become so long that each brush might always cause a spark discharge between the electrodes. Thus considering, it will be seen that a spark discharge is always preceded by a preliminary brush, and that the former occurs along the path made by the latter as was observed by B. Walter.

If the spark discharge takes place in such a manner, the path of a spark will be different in its form according as it was formed along a positive brush or along the negative. This was really the case, and illustrated by Fig. 2 and Fig. 3. Fig. 2 is the photograph of a spark which passed between a plane cathode and a spherical anode of 1.7 centimetre in diameter of an influence machine, and Fig. 3 was taken when the signs of the poles were reversed. The distance between the electrode was the same in both cases and was about four centimetres. As is evident from these figures, the zigzag spark in Fig. 2 is very different from the rather smooth spark in Fig. 3. This difference of the nature of spark in the two cases seems to be explained easily by the consideration that the zigzag spark in Fig. 2 took place along an irregular positive brush which would have appeared previously at the spherical anode, and that the smooth spark in Fig. 3 occurred along a regular negative brush which would have appeared also previously at the spherical cathode.

When special attention was not paid to avoid the formation of either of the two kinds of brushes, positive and negative brushes appeared generally at each electrode respectively. Among these the irregular fine positive brush is, in most cases, much longer than the diffuse negative brush as was stated and explained before. If a spark discharge occurs in such cases, a major part of its path will be along a zigzag branch of a preliminary positive brush. The zigzag nature of a spark seems thus to be due to this nature of a positive brush.

Now, it is well known that when a spark is branched, the branches point to the negative electrode, as was observed in the case of the spark in the laboratory or in that of the lightning spark. This mode of branching of the spark is entirely identical with that of the

positive brush. And the branches of the spark may be regarded as those of its preliminary positive brush.

If the electrodes are not of the same size, the spark length for the same potential difference depends upon whether the larger or smaller electrode is used as the cathode. Thus, for example, Faraday found that the spark length was larger when the smaller sphere was positive than when it was negative. More recently Villard and Abraham¹, on experimenting with the electrodes of a plane and a sphere of various diameters, found that the spark length was larger when the sphere was positive than when it was negative. This may be explained by the consideration that the spark is formed along the path made by a preliminary brush discharge, and that a positive brush is more favorable by its longer extension for the formation of the spark than a negative brush.

Contrary to the case above mentioned, K. Wesendonck² observed that, in the case of a pure spark where no trace of a brush or a glow was detected, the effect of the dissimilarity of the two electrodes on the spark length was absent. This seems to the writers to be the effect of a large capacity which K. Wesendonck applied between the electrodes to avoid the appearance of any other form of discharge than spark. But, a further investigation is of course needed on this point.

Lastly it is especially interesting to note that the sparking potential between the electrodes is higher when a spark occurs in a state of positive glow discharge at the surface of the anode than when it takes place in a state of positive brush discharge or in that of a non-luminous discharge at the anode as was observed by M. Toepler³ and Villard and Abraham⁴. According to the writers' view, the spark which takes place in a state of glow discharge at the anode is also preceded by the appearance of a positive brush, and the spark passes along the path made by this preliminary positive brush. It has been already mentioned that a positive brush which appeared in a state of positive glow at the anode started at a "luminous point" in the glow at the anode; and this "luminous point" was considered, in that case, to be due to the ionisation by collisions of positive ions with the molecules of the air. When a positive brush did not accompany

¹ Villard and Abraham, *C.R.*, **153**, p. 1200, (1911).

² K. Wesendonck, *Wied. Ann.*, **38**, p. 222, (1889).

³ M. Toepler, *Drude Ann.*, **7**, p. 477 (1902).

⁴ Villard and Abraham, *C.R.*, **130**, p. 1286, (1910).

a positive glow, the ionisation by collisions of positive ions with air molecules which took place in a stronger part of the brush, was considered to be caused by the fact that the electric field in every portion of a weaker part of the brush was strengthened by the accumulation of many positive and negative ions and electrons in a narrow space. Now, in the case of a "luminous point" in the positive glow, this condition is absent, and a higher potential difference between the electrodes was needed to cause the ionisation by collisions of positive ions with air molecules in a portion of the positive glow, that is to form a "luminous point" in the glow which was a "Zündstoff eines Funkens" as was named by K. Wesendonk.

Summary.

1. The natures of a positive and a negative brush discharge, and especially the parts played by them in the formation of a spark discharge were investigated.

2. The stronger part and the weaker part of a positive brush were different in their natures. The latter was a pilot of the former, and the arrival of the end of the former at the cathode or at a negative brush caused a spark discharge between the electrodes.

3. An explanation of the formation of the negative and the positive brush was undertaken by the consideration of the ionisation by collisions of electrons and of positive ions with the molecules of the air.

4. The conditions under which the positive glow was formed were examined, and it was observed that a uniform supply of a great number of electrons toward the anode was favorable for the formation of the positive glow.

5. A positive brush which appeared at the anode in a state of positive glow discharge was observed to start at a "luminous point" in the positive glow. As a spark took place along a preliminary brush discharge, this "luminous point" was also the starting point of the spark at the anode, and this "luminous point" was called by K. Wesendonk "der Zündstoff eines Funkens."

6. An explanation of the various features of a spark discharge was attempted on the ground that a spark passed between the electrodes along the path made by a preliminary brush.

The writers' hearty thanks are due to Prof. T. Mizuno for his interest in this research.

Fig. 1.



Fig. 2.



Fig. 3.



Hydrates of Aluminium Nitrate.

BY

Kenzo Inamura.

(Received July 5, 1919)

Of aluminium nitrate, the hydrate with 18 molecules of water, $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$, is most well known, but, in addition, the hydrates with less molecules of water have also been described. Recently, Z. Jovitschitsch¹ obtained a new hydrate in snow-white prisms by heating ignited alumina with concentrated nitric acid (sp. gr. 1.4) and he gave it the formula, $\text{Al}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$, from the analysis of a single sample. Then, R. Seligman and P. Williams obtained three hydrates under different conditions, and their conclusions were as follows:²

"Aluminium nitrate may crystallise in at least three forms, and the compositions of two of these have been determined as $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$ and $\text{Al}_2(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$. The third hydrate probably crystallises with 15 or 16 molecules of water. The hydrate containing $12\text{H}_2\text{O}$ does not appear to have been discovered hitherto.

"The hydrate containing $18\text{H}_2\text{O}$ is the most stable form at 20° in nitric acid having D1.42 and is the least soluble.

"In acid having D1.5 at 20° the hydrate containing $12\text{H}_2\text{O}$ is alone stable.

"The hydrate containing 15 or $16\text{H}_2\text{O}$ is stable in an acid of intermediate strength."

¹ Monatsh. Chem., **33**, 16 (1912).

² J. Chem. Soc., **109**, 612 (1916).

The authors could not definitely determine the composition of the intermediate hydrate on account of the difficulty of drying it.

Now the writer, on the suggestion of Prof. Y. Osaka, took up the systematic study of the hydrates of aluminium nitrate from the standpoint of the phase rule, taking aluminium nitrate, nitric acid, and water as the components.

The materials used in the investigation were prepared in the following way :

Aluminium nitrate. Aluminium hydroxide was precipitated from a solution of purified alum with ammonia, washed well with water until it was free from sulphuric acid radical. It was dissolved in excess of nitric acid of sp. gr. 1.375 and the solution was evaporated. Crystals of the hydrate with $18\text{H}_2\text{O}$ were obtained and were recrystallised from nitric acid.

Nitric acid. Nitric acid of sp. gr. 1.375 of the Jap. Pharm. was mixed with about an equal volume of concentrated sulphuric acid and distilled under atmospheric pressure. The acid thus obtained was somewhat coloured with nitrous fumes, which were removed by passing dry air through it under slight warming. To obtain a more concentrated acid, concentrated sulphuric acid was added again to about an equal volume of the prepared acid and the mixture was distilled under a reduced pressure of about 30 mm. mercury. This was almost colourless. To remove traces of the sulphuric acid which happened to contaminate it by accident, it was redistilled with some barium nitrate under reduced pressure as before.

Water. The ordinary distilled water was used.

The experiments were carried out in the following way: The three components were mixed in different proportions in an Erlenmeyer flask with a well ground stopper, of a capacity of about 50 cc. The flask was made to rotate in a thermostat of 25.0° for one or two days. When equilibrium was attained, the solution and the residue were separated by filtration through asbestos. During the process a loss of a minute quantity of nitric acid was unavoidable. The residue was pressed between folded filter paper to remove the mother liquor as much as possible.

For experiments when more concentrated acid was required, the hydrate with $18\text{H}_2\text{O}$ was dehydrated before use. For this purpose,

it was fused on a water-bath and gave a white mass. It was powdered and dried in a steam-bath for about 10 hours. On analysis it was found to have lost some nitric acid and had the composition corresponding to the formula, $\text{Al}_2\text{O}_3 \cdot 2(\text{N}_2\text{O}_5) \cdot 9\text{H}_2\text{O}$. Thus, although the acid was concentrated as much as 96 per cent., it was impossible to study the equilibrium in an acid solution more concentrated than 90.51 per cent.

The solutions and residues were analysed in the following way:

Aluminium was determined as alumina by igniting aluminium nitrate to a constant weight.

Nitric acid was determined according to the method of Schlösing and Grandeau, improved by Tiemann and Schulze,¹ by estimating the volume of nitric oxide produced by decomposing nitrate with ferrous chloride and hydrochloric acid.

Water was estimated by difference.

The results of the analyses are reproduced in Table 1, from which Table 2 was prepared.

¹ Treadwell—Hall, *Analyt. Chem.*, II, 456 (1914).

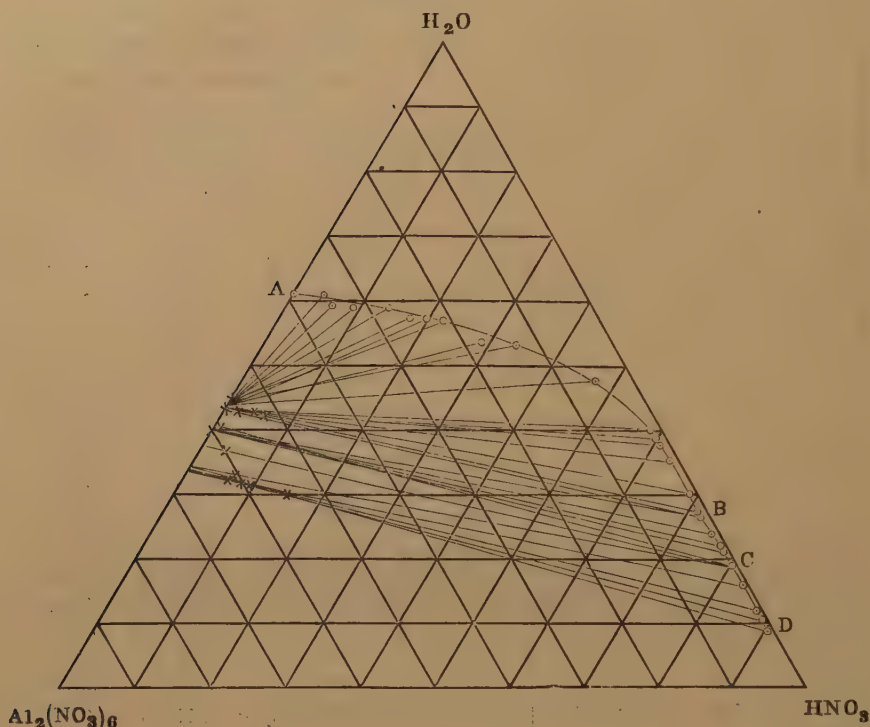
TABLE I.

No.	Solution.			Residue wet with some solution.		
	Al ₂ O ₃	N ₂ O ₅	H ₂ O	Al ₂ O ₃	N ₂ O ₅	H ₂ O
	(in gram percentages.)			(in gram percentages.)		
1	9.32	29.27	61.41	13.57	41.79	44.64
2	9.36	29.81	60.83	13.63	41.15	45.22
3	8.32	29.99	61.69	13.58	41.97	44.45
4	8.21	31.30	60.49	13.61	42.05	45.34
5	7.71	32.29	60.00	13.54	42.80	45.61
6	6.53	32.41	61.06	13.12	41.70	45.18
7	6.06	33.95	59.98	13.41	42.83	43.76
8	5.44	34.37	60.19	13.47	42.85	43.68
9	4.98	34.53	60.49	13.23	42.36	44.41
10	4.21	37.91	57.88	13.34	42.78	43.38
11	3.16	38.72	58.12	13.25	42.80	43.95
12	1.21	44.19	54.60	13.05	42.67	44.28
13	0.44	51.33	48.23	13.20	43.49	43.31
14	0.38	52.40	47.22	12.76	43.98	43.26
15	0.34	52.87	46.79	12.73	43.22	44.05
16	0.32	55.16	44.52	13.14	43.62	43.24
17	0.23	59.73	40.04	12.79	43.51	43.70
18	0.30	61.93	37.77	12.53	44.89	42.58
19	0.26	62.28	37.46	13.39	43.62	42.99
20	0.30	62.66	37.04	12.80	45.03	42.17
21	0.30	62.70	37.00	13.31	43.73	42.96
22	0.22	62.81	36.97	14.44	45.25	40.31
23	0.17	65.10	34.73	14.31	45.62	40.07
24	0.11	66.26	33.63	14.25	45.13	40.62
25	0.11	67.02	32.87	14.32	45.44	40.24
26	0.07	67.32	32.61	14.48	45.89	39.63
27	0.06	68.97	30.97	14.13	46.23	39.64
28	0.06	69.42	30.52	14.30	48.51	37.19
29	0.04	69.61	30.35	14.49	51.41	34.10
30	0.02	71.49	28.49	14.78	52.03	33.19
31	0.04	75.46	24.50	14.20	53.20	32.60
32	0.04	75.78	24.18	14.15	53.23	32.62
33	0.05	76.31	23.64	14.39	52.50	33.11
34	0.06	76.47	23.47	14.21	52.16	33.63
35	0.08	76.99	22.93	14.07	52.89	31.04
36	0.10	77.75	22.33	13.25	54.51	32.24

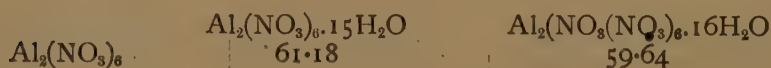
TABLE 2.

No.	Solution.			Residue wet with some solution.		
	$\text{Al}_2(\text{NO}_3)_6$	HNO_3	H_2O	$\text{Al}_2(\text{NO}_3)_6$	HNO_3	H_2O
	(in gram percentages.)			(in gram percentages.)		
A 1	38.87	—0.33	—	56.60	—1.45	—
2	39.04	0.15	60.81	56.85	—2.42	—
3	34.70	4.21	61.09	56.64	—1.27	—
4	34.24	6.15	59.61	56.77	—1.30	—
5	32.16	9.15	58.69	56.47	—0.15	—
6	27.23	13.67	59.10	54.72	0.12	45.16
7	25.32	17.15	57.53	55.93	0.36	43.71
8	22.69	19.97	57.34	56.18	0.16	43.66
9	20.77	21.86	57.37	55.19	0.47	44.34
10	17.57	28.65	53.78	55.65	0.06	44.29
11	13.18	33.49	53.33	55.27	0.91	43.82
12	5.05	47.08	47.87	54.42	1.52	44.06
13	1.84	58.26	39.90	55.06	1.90	43.04
14	1.59	59.73	38.68	53.23	4.10	42.67
15	1.42	60.43	38.15	53.09	3.34	43.57
16	1.34	63.17	35.49	54.81	2.28	42.91
17	0.97	68.84	30.19	53.35	3.44	43.21
18	1.25	71.15	27.60	52.26	6.02	41.72
19	1.08	71.71	27.21	55.85	1.35	42.80
20	1.25	72.01	26.74	53.29	5.30	41.41
B 21	1.25	72.06	26.69	55.52	1.77	42.71
22	0.92	72.47	26.61	60.24	—0.64	—
23	0.71	75.34	23.95	59.68	0.29	40.03
24	0.45	76.91	22.64	59.44	—0.07	—
25	0.46	77.80	21.74	59.72	0.05	40.23
26	0.28	78.31	21.41	60.38	—0.01	—
27	0.24	80.28	19.48	58.93	1.67	41.07
C 28	0.24	80.58	19.18	59.64	3.70	36.66
29	0.17	81.08	18.75	60.44	6.37	33.19
30	0.08	83.35	16.57	61.65	6.02	32.33
31	0.17	87.66	12.17	59.23	9.53	31.24
32	0.18	88.26	11.56	59.01	9.77	31.22
33	0.21	88.86	10.93	60.01	8.03	31.96
34	0.25	89.02	10.73	59.27	8.29	32.44
35	0.34	89.54	10.12	58.68	9.66	31.66
D 36	0.43	90.12	9.45	55.27	14.57	30.16

FIG. 1.

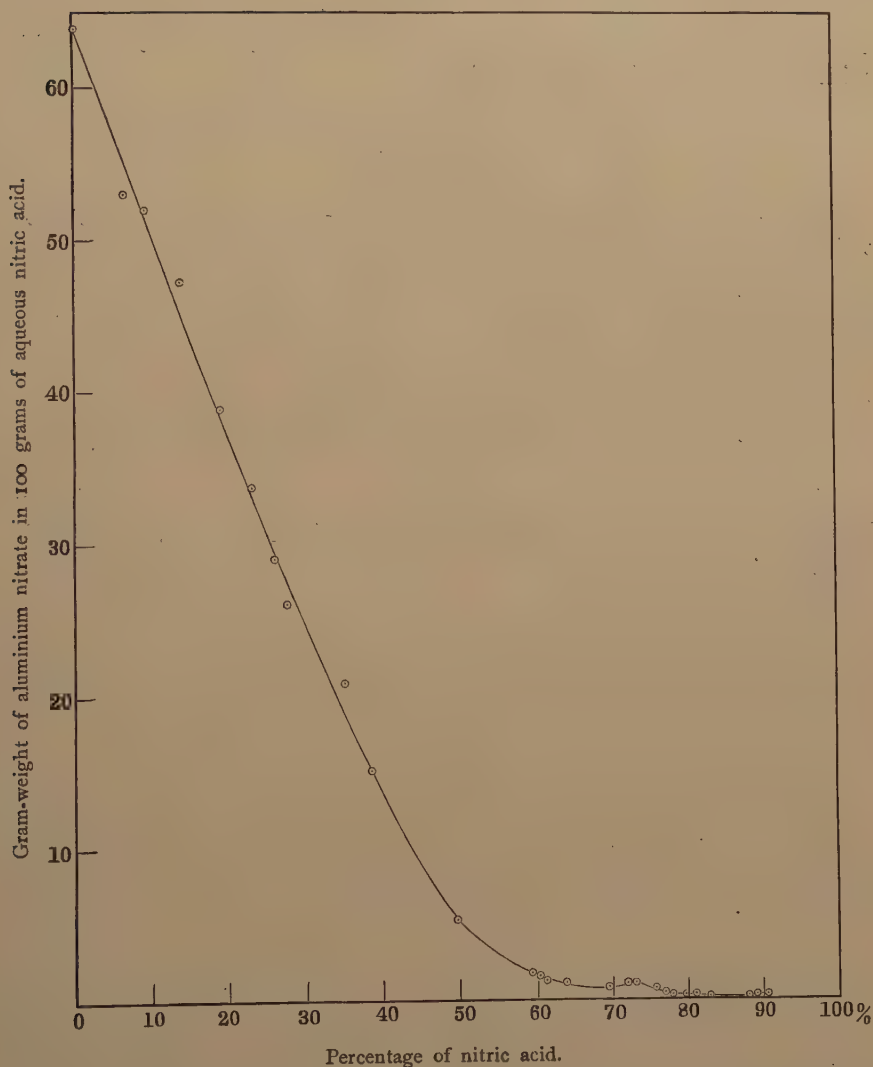


The data in Table 2 are graphically represented in Fig. 1, referring to a triangular coordinate. The point A represents the saturated solution of aluminium nitrate with $18\text{H}_2\text{O}$ in water. In the solutions from A to B the residue is $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$ [$(\text{Al}_2(\text{NO}_3)_6:\text{H}_2\text{O} = 56.78:43.23)$]. At the point B the concentration of the acid is about 73 per cent. (sp. gr. 1.435 at 15°). In the solution from B to C, the residue seems to have $16\text{H}_2\text{O}$ rather than $15\text{H}_2\text{O}$, as the percentages of aluminium nitrate in them are as follows:



In the solution from C to D, the residue is $\text{Al}_2(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$ [$(\text{Al}_2(\text{NO}_3)_6:\text{H}_2\text{O} = 66.33:33.67)$]. At the point D the percentage of the acid is 90.51 (sp. gr. 1.497 at 15°).

FIG. 2.



The hydrate with $16\text{H}_2\text{O}$ was obtained as very fine needles, but that with $12\text{H}_2\text{O}$ as a fine powder only.

Solubilities of aluminium nitrate in nitric acid of different concentrations are shown in Fig. 2, the percentage of nitric acid and gram-weight of aluminium nitrate in 100 grams of aqueous nitric acid being taken as coordinates. Naturally the curve consists of three parts, each corresponding to a particular hydrate. As clearly seen from the

figure, the solubility of aluminium nitrate decreases very rapidly when the concentration of the acid is increased until the acid is about 60 per cent. Thenceforward, the solubility is only slightly changed with the concentration of the acid.

CONCLUSION.

At 25.0° three kinds of hydrates of aluminium nitrate may crystallise out stably from nitric acid of proper concentrations.

The hydrate with $18\text{H}_2\text{O}$ is stable in acid solution below 73 per cent. (sp. gr. 1.435 at 15°).

The hydrate with $16\text{H}_2\text{O}$ is stable in acid between 73 and 81 per cent. (sp. gr. 1.435—1.463 at 15°).

The hydrate with $12\text{H}_2\text{O}$ is stable in acid above 81 per cent.

The writer wishes to express his thanks to Professor Osaka for his suggestion of the work and for the kind interest he has taken in the experiment throughout.

Notes on the Normalities of Standard Solutions.

By

Yukichi Osaka.

(Received Oct. 14, 1919.)

In volumetric analysis, much attention is usually not paid to the change of the normality of standard solutions by variation of room temperature, but as the exactness of a volume measurement with a pipette is about 0.5% of its content, and with a measuring flask, the error may be less than that amount,¹⁾ it is possible to increase the exactness of a volumetric analysis by applying a proper correction to the change of normality by variation of room temperature, if the latter causes any more change in the former than the extent of the said exactness of measurement. For this correction, P. Casamajor²⁾ put the change of standard solutions to be equal to that of pure water. As this, however, is not applicable to all standard solutions, A. Schultze³⁾ measured the thermal expansion of various standard solutions by the dilatometer method at every fifth degree from 5° to 30°. He put the volume at 0° as 1.0000000 and estimated graphically the volume at each temperature from 0° to 30°. He took the temperature of 17.5° as the standard temperature, and taking the thermal expansion of glass also into consideration, calculated the volume of water to be added to the normal solution prepared at room temperature to make it exactly normal at the standard temperature.

¹ Ostwald-Luther, Hand- und Hilfsbuch z. Ausf. physiko-chemi. Messungen, 3. Aufl., 166, 176.

² Chem. News, 35, 1160 (1877).

³ Zs. anal. Chem., 21, 167 (1882).

Then Schlösser¹ using Schultze's data, taking 15° and also 20° as the standard temperatures, worked out a table to show how much greater or less a given volume is at different temperatures than it would be at the standard temperatures.

K. Inamura² measured the densities of some standard solutions, by using a Sprengel-Ostwald pyknometer, at every fifth degree from 5° to 35° and taking 20° as the standard temperature, calculated the normalities at other temperatures which would be exactly normal at the standard temperature.

Now, the writer has calculated new tables, practically convenient, using the data given by Schultze and by Inamura, and taking as the standard temperature 15°, 20°, and 25° successively.

Let d be the density of a solution at the standard temperature t and d' be that at another temperature t' , then a normal solution at t would be d'/d normal at t' . The ratio d'/d for different solutions, referring to the three standard temperatures, is given in Column I of Tables I to 16.

For the correction of the thermal expansion of glass the capacity of a glass vessel was taken to be calibrated for that volume named on it at 15°, and the cubical expansion coefficient of glass to be 0.000029. A normal solution at t is d'/d normal at t' and the capacity of a litre-flask at that temperature is 1 litre $\times (1 + 0.000029 (t - 15))$. Thus the amount of the solute required for the preparation of its normal solution at t , which would be exactly normal at t , is not 1 gram-equivalent, but $(1 + 0.000029 (t - 15)) d'/d$. This value is given in Column II of Tables I to 16 for each of the three standard temperatures.

In these tables, the normality of all standard solutions at the respective standard temperatures was denoted by 1.00000; so in the case of decinormal solutions, the values given in the tables are to be divided by 10, and in the case of centinormal solutions by 100. For comparison a similar table was constructed for pure water. The tables marked* are based on Inamura's data and all the others on Schulze's.

¹ Chem. Zg., 29, 509 (1905).

² Report, No. 59 (1917) of the Kure Naval Explosive Research Laboratory, communicated by T. Nakatani.

TABLE I.
Oxalic Acid : Normal.

Temp.	Standard temp.	15°		25°		25°	
		I	II	I	II	I	II
5°		1.00160	1.00131	1.00279	1.00250	1.00422	1.00393
6		149	123	267	241	411	385
7		137	114	255	232	399	375
8		124	103	242	222	386	365
9		110	092	228	211	372	354
10		095	080	213	198	356	342
11		078	066	196	185	340	328
12		060	051	178	170	322	313
13		041	035	159	153	302	297
14		021	018	139	136	282	279
15		1.00000	1.00000	118	118	262	262
16		0.99978	0.99981	096	099	239	242
17		955	960	073	079	216	222
18		931	940	050	058	193	201
19		907	919	025	037	169	180
20		882	896	1.00000	1.00014	143	158
21		854	872	0.99973	0.99990	116	133
22		828	848	946	966	089	109
23		799	822	917	940	060	083
24		769	795	887	913	030	056
25		739	768	857	886	1.00000	029
26		708	740	826	858	0.99969	1.00001
27		677	712	795	830	938	0.99973
28		646	683	764	801	906	944
29		613	654	731	771	874	914
30		580	623	698	741	840	884

TABLE 2.*
Oxalic Acid : $\frac{1}{10}$ Normal.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1.00078	1.00049	1.00161	1.00132	1.00270	1.00241
6		74	48	158	131	267	240
7		68	46	152	130	263	238
8		62	43	147	127	256	234
9		55	40	140	123	249	230
10		49	35	132	120	242	227
11		40	30	124	114	234	222
12		30	24	115	109	224	216
13		21	18	105	102	214	209
14		10	10	095	094	203	201
15		1.00000	1.00000	083	083	192	192
16		0.99985	0.99990	067	073	180	181
17		970	978	051	060	164	170
18		954	964	035	047	146	155
19		936	949	018	033	128	140
20		918	931	1.00000	1.00015	109	124
21		897	913	0.99980	0.99998	087	107
22		876	897	959	982	066	090
23		854	880	937	962	044	070
24		831	860	914	943	022	050
25		806	837	891	920	1.00000	029
26		782	814	866	900	0.99974	1.00006
27		756	792	840	880	948	0.99983
28		730	770	813	854	921	960
29		702	744	785	830	894	936
30		674	713	757	801	866	910

TABLE 3.
Hydrochloric Acid : Normal.

Temp.	Standard temp.		15°		20°		25°	
			I	II	I	II	I	II
5°			1·00153	1·00124	1·00264	1·00235	1·00395	1·00366
6			142	116	253	227	385	359
7			131	108	242	219	374	350
8			118	098	229	209	361	340
9			103	087	215	197	346	329
10			089	075	200	185	331	317
11			073	062	184	172	315	304
12			056	048	167	158	298	290
13			038	034	149	143	280	275
14			020	017	130	127	261	259
15			1·00000	1·00000	111	111	242	242
16			0·99980	0·99983	090	093	221	224
17			958	964	069	074	200	206
18			936	944	046	055	177	186
19			913	924	023	035	154	166
20			890	904	1·00000	015	131	146
21			865	882	0·99975	0·99993	106	124
22			841	861	951	971	082	102
23			814	838	925	948	056	079
24			787	813	898	924	029	055
25			759	788	869	898	1·00000	029
26			730	761	840	872	0·99971	1·00003
27			700	735	811	845	942	0·99976
28			670	708	780	818	911	949
29			639	679	749	789	880	920
30			608	651	718	761	849	892

TABLE 4.
Nitric Acid : Normal.

Temp.	Standard temp.		15°		20°		25°	
			I	II	I	II	I	II
5°			1·00227	1·00198	1·00371	1·00342	1·00534	1·00504
6			209	183	353	327	516	489
7			189	166	333	310	496	473
8			168	148	312	292	475	455
9			147	130	291	274	454	436
10			125	110	269	254	431	416
11			102	090	246	234	408	396
12			077	069	221	212	384	375
13			052	046	196	190	358	352
14			026	023	170	167	332	329
15			1·00000	1·00000	144	144	306	306
16			0·99973	0·99975	116	119	279	281
17			945	950	088	094	251	256
18			916	925	059	068	222	230
19			886	898	030	041	192	204
20			857	871	1·00000	1·00014	162	177
21			826	844	0·99970	0·99987	132	149
22			795	815	938	958	100	120
23			762	785	905	928	067	090
24			729	755	872	898	034	060
25			695	724	838	867	1·00000	1·00029
26			660	692	803	835	0·99965	0·99996
27			624	659	767	802	929	964
28			588	626	731	768	893	930
29			551	592	694	735	856	897
30			516	559	658	702	820	863

TABLE 5.
Sulphuric Acid : Normal.

Standard temp. Temp.	15°		20°		25°	
	I	II	I	II	I	II
5°	1·0221	1·00192	1·00365	1·00336	1·00526	1·00496
6	204	178	348	322	508	482
7	185	162	328	305	489	465
8	165	144	309	288	469	448
9	144	126	287	270	448	430
10	122	108	266	251	426	411
11	099	088	243	232	403	392
12	076	067	220	211	380	371
13	051	045	195	189	355	349
14	026	023	169	166	329	327
15	1·00000	1·00000	144	144	304	304
16	0·99972	0·99975	116	119	276	279
17	945	951	089	095	249	255
18	916	925	060	068	220	228
19	887	899	031	042	191	202
20	857	871	1·00000	1·00015	160	174
21	827	844	0·99970	0·99987	130	147
22	796	816	939	960	099	119
23	764	788	907	931	067	091
24	731	757	874	900	034	060
25	697	726	840	869	1·00000	1·00029
26	663	694	806	837	0·99965	0·99997
27	627	662	770	805	929	964
28	590	628	733	771	893	930
29	554	594	697	737	856	897
30	516	559	659	702	818	862

TABLE 6.
Sodium Carbonate : Normal.

Standard temp. Temp.	15°		20°		25°	
	I	II	I	II	I	II
5°	1·00230	1·00201	1·00374	1·00345	1·00534	1·00505
6	211	185	355	329	515	489
7	191	168	334	311	494	471
8	169	149	313	292	472	452
9	147	130	291	273	450	433
10	125	110	268	253	428	413
11	101	089	244	233	404	392
12	077	068	220	211	380	371
13	053	047	196	190	355	349
14	026	024	170	167	329	326
15	1·00000	1·00000	143	143	303	303
16	0·99973	0·99976	116	119	276	278
17	945	951	088	094	247	253
18	916	925	059	068	219	227
19	887	899	030	041	189	201
20	857	872	1·00000	1·00014	159	174
21	826	844	0·99969	0·99987	129	146
22	795	816	938	958	097	118
23	764	787	907	930	066	089
24	733	758	875	901	034	060
25	698	727	841	870	1·00000	1·00029
26	664	696	807	840	0·99966	0·99997
27	630	665	773	807	982	966
28	595	632	737	775	896	934
29	558	599	701	741	860	900
30	521	564	664	707	822	866

TABLE 7.*
Sodium Carbonate : $\frac{1}{10}$ Normal.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1.00095	1.00065	1.00177	1.00148	1.00287	1.00258
6		90	63	172	146	281	256
7		84	60	166	142	275	252
8		76	56	159	138	269	248
9		67	50	151	132	260	243
10		58	44	141	126	251	236
11		49	38	132	119	241	229
12		38	30	120	111	230	220
13		26	20	109	103	219	211
14		13	10	96	94	205	202
15		1.00000	1.00000	0.82	0.82	192	192
16		0.99986	0.99990	0.69	0.70	177	181
17		971	978	053	059	161	170
18		955	964	037	046	145	155
19		938	949	019	031	128	140
20		918	932	1.00000	1.00015	110	124
21		897	916	0.99980	0.99999	090	108
22		876	899	959	982	070	091
23		854	880	936	962	049	072
24		831	860	914	941	025	051
25		808	837	890	919	1.00000	029
26		782	812	865	898	0.99975	1.00006
27		756	791	840	875	950	0.99983
28		730	769	813	851	924	960
29		703	745	785	826	896	935
30		675	718	757	800	866	910

TABLE 8.
Sodium Hydroxide : Normal.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1.00245	1.00216	1.00393	1.00364	1.00559	1.00530
6		224	198	372	346	538	512
7		202	179	350	327	516	492
8		180	159	327	307	493	473
9		155	138	303	286	469	452
10		131	116	279	264	445	430
11		107	95	255	243	421	409
12		081	073	229	221	395	386
13		055	050	203	197	369	363
14		028	025	176	173	341	339
15		1.00000	1.00000	148	148	313	313
16		0.99972	0.99975	120	123	285	288
17		944	949	091	097	257	263
18		914	923	062	070	227	236
19		884	895	032	043	197	209
20		852	867	1.00000	1.00015	165	180
21		821	839	0.99969	0.99986	134	152
22		789	809	937	957	102	122
23		756	779	903	926	068	091
24		722	748	869	895	034	060
25		688	716	835	864	1.00000	1.00029
26		653	685	801	832	0.99966	0.99997
27		617	652	765	799	930	964
28		582	619	729	766	894	931
29		546	586	693	733	858	898
30		508	551	655	698	819	863

TABLE 9.
Sodium Chloride: $\frac{1}{10}$ Normal.

Standard temp.	15°		20°		25°	
Temp.	I	II	I	II	I	II
5°	1.00108	1.00078	1.00201	1.00172	1.00321	1.00291
6	102	75	196	170	315	289
7	095	72	189	165	308	285
8	087	72	180	160	300	279
9	077	66	171	153	290	273
10	067	60	160	146	280	265
11	056	52	149	137	269	257
12	043	44	137	128	256	248
13	030	35	123	118	243	237
14	016	24	109	106	229	226
15	1.00000	1.00013	093	093	213	213
16	0.99984	0.99987	077	080	196	199
17	966	971	059	065	178	184
18	946	955	040	049	159	168
19	927	938	021	032	140	151
20	907	921	1.00000	1.00015	119	134
21	888	906	0.99982	0.99999	101	118
22	861	882	955	975	074	094
23	838	861	931	954	050	074
24	813	839	906	932	025	051
25	788	817	881	910	1.00000	029
26	761	792	857	888	0.99973	1.00005
27	732	767	826	860	945	0.99979
28	703	741	796	834	915	953
29	672	713	766	806	884	925
30	642	685	735	778	854	897

TABLE 10.
Sodium Chloride: $\frac{1}{100}$ Normal.

Standard temp.	15°		20°		25°	
Temp.	I	II	I	II	I	II
5°	1.00089	1.00060	1.00178	1.00149	1.00295	1.00265
6	85	59	174	148	290	264
7	80	57	169	146	285	262
8	75	55	164	143	280	260
9	69	51	158	140	274	256
10	61	46	150	135	266	251
11	51	40	140	128	256	245
12	40	31	129	120	245	236
13	28	22	117	111	233	227
14	15	12	103	100	220	217
15	1.00000	1.00000	1.00089	089	205	205
16	0.99985	0.99988	74	077	190	193
17	969	974	57	063	173	179
18	950	958	39	047	155	164
19	931	942	20	031	136	147
20	911	926	1.00000	1.00015	116	131
21	890	907	0.99978	0.99996	094	112
22	868	888	956	976	072	093
23	845	868	933	957	050	073
24	821	847	909	936	026	052
25	796	824	884	913	1.00000	029
26	769	800	857	889	0.99973	1.00005
27	740	774	828	863	944	0.99979
28	710	748	798	836	914	952
29	680	720	768	809	884	925
30	649	693	738	781	853	897

TABLE II.
Silver Nitrate : $\frac{1}{10}$ Normal.

Standard temp.	15°		20°		25°	
Temp.	I	II	I	II	I	II
5°	1.00105	1.00076	1.00202	1.00173	1.00321	1.00292
6	099	73	196	170	315	289
7	093	69	189	166	309	286
8	085	65	182	161	301	281
9	077	60	174	156	294	276
10	068	53	164	150	284	269
11	056	44	153	141	272	260
12	044	35	141	132	260	251
13	031	25	128	122	247	241
14	016	13	113	110	232	229
15	1.00000	1.00000	097	097	216	216
16	0.99983	0.99986	080	083	199	202
17	965	971	062	068	181	187
18	946	954	042	051	162	170
19	925	937	022	033	141	153
20	904	918	1.00000	1.00015	119	134
21	882	900	0.99979	0.99996	098	116
22	859	880	956	976	075	096
23	835	859	932	955	051	076
24	811	837	907	933	027	053
25	784	813	881	910	1.00000	029
26	757	789	854	885	0.99973	1.00005
27	730	764	826	861	945	0.99980
28	700	737	796	833	915	953
29	670	710	766	807	885	926
30	640	683	737	780	856	899

TABLE 12.
Silver Nitrate : $\frac{1}{100}$ Normal.

Standard temp.	15°		20°		25°	
Temp.	I	II	I	II	I	II
5°	1.00089	1.00059	1.00177	1.00148	1.00294	1.00265
6	86	60	175	148	291	265
7	82	58	170	147	287	263
8	76	55	164	144	281	260
9	69	52	158	140	274	257
10	60	46	149	134	266	251
11	50	39	139	127	255	244
12	39	31	128	119	244	236
13	28	22	116	111	233	227
14	15	12	104	101	220	217
15	1.00000	1.00000	089	089	205	205
16	0.99984	0.99987	073	076	189	192
17	968	973	056	062	172	178
18	950	958	038	047	155	163
19	931	942	020	031	136	147
20	911	926	1.00000	1.00015	116	131
21	891	908	0.99979	1.99997	095	113
22	868	888	956	977	073	093
23	846	869	934	957	050	074
24	821	847	909	935	025	051
25	795	824	884	913	1.00000	029
26	770	801	858	890	0.99974	1.00006
27	742	777	831	865	947	0.99981
28	715	752	803	841	919	957
29	686	726	774	815	890	931
30	655	698	743	787	859	903

TABLE 13.
Potassium Permanganate: $\frac{1}{10}$ Normal.

Standard temp.	15°		20°		25°	
Temp.	I	II	I	II	I	II
5°	1.00096	1.00069	1.00193	1.00164	1.00312	1.00283
6	93	67	187	161	307	281
7	89	66	183	160	302	279
8	82	62	176	156	295	275
9	74	57	168	151	288	270
10	65	51	159	145	279	264
11	54	43	149	137	268	256
12	42	34	137	128	256	247
13	29	23	123	117	243	237
14	15	12	109	106	228	225
15	1.00000	1.00000	094	094	213	213
16	0.99984	0.99986	078	080	197	200
17	966	972	060	066	179	185
18	947	955	041	049	160	169
19	927	938	021	032	140	151
20	906	921	1.00000	1.00015	119	134
21	885	902	0.99979	0.99996	098	115
22	862	882	956	976	075	095
23	838	861	932	955	051	074
24	813	839	907	933	026	052
25	787	816	881	910	1.00000	029
26	760	792	854	886	0.99973	1.00005
27	732	766	826	861	945	0.99980
28	703	741	797	835	916	953
29	674	714	767	808	886	927
30	643	686	737	780	856	899

TABLE 14.
Potassium Permanganate: $\frac{1}{100}$ Normal.

Standard temp.	15°		20°		25°	
Temp.	I	II	I	II	I	II
5°	1.00087	1.00058	1.00181	1.00151	1.00294	1.00264
6	84	58	178	151	291	264
7	80	57	173	150	286	263
8	75	55	168	148	283	263
9	68	51	161	144	274	257
10	60	46	154	139	266	252
11	51	39	143	132	256	245
12	40	31	133	124	246	237
13	28	23	121	116	234	229
14	15	12	108	105	220	218
15	1.00000	1.00000	093	093	206	206
16	0.99983	0.99986	076	079	189	192
17	966	971	058	064	171	177
18	947	956	040	049	153	162
19	928	939	020	032	133	145
20	907	922	1.00000	1.00015	113	127
21	886	904	0.99979	0.99996	092	109
22	864	885	957	977	070	090
23	842	865	935	958	048	071
24	819	845	912	937	024	050
25	795	823	887	916	1.00000	029
26	769	801	862	894	9.99975	1.00006
27	742	777	835	870	947	0.99982
28	713	751	806	843	918	956
29	684	724	777	817	889	930
30	653	696	745	789	858	901

TABLE 15.
Ammonium Thiocyanate : $\frac{1}{10}$ Normal.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1.00104	1.00075	1.00199	1.00170	1.00322	1.00292
6		100	74	194	168	317	291
7		093	70	188	165	311	287
8		086	66	181	161	304	283
9		078	61	173	155	295	278
10		068	53	163	148	285	271
11		057	45	151	140	274	262
12		044	36	139	130	261	253
13		031	25	125	119	248	242
14		016	13	111	108	233	230
15		1.00000	1.00000	094	094	217	217
16		0.99983	0.99986	078	081	200	203
17		966	972	060	066	183	189
18		946	955	040	049	163	172
19		926	937	021	032	143	154
20		906	920	1.00000	1.00015	122	137
21		883	900	0.99977	0.99995	100	117
22		860	880	954	974	076	097
23		835	858	930	953	052	075
24		810	836	904	930	027	053
25		783	812	878	907	1.00000	029
26		756	788	851	882	0.99973	1.00005
27		728	763	822	857	945	0.99979
28		699	737	793	831	916	953
29		669	710	764	804	886	926
30		639	683	734	777	856	899

TABLE 16.
Water.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1.00083	1.00054	1.00174	1.00144	1.00288	1.00259
6		81	55	171	145	286	260
7		77	54	168	144	282	259
8		73	52	163	143	277	257
9		66	49	157	139	271	254
10		59	44	149	134	263	249
11		49	38	140	128	254	243
12		39	30	129	120	244	235
13		27	21	117	112	232	226
14		14	11	104	101	219	216
15		1.00000	1.00000	090	090	205	205
16		0.99984	0.99987	074	077	189	192
17		968	974	058	064	173	178
18		949	958	040	048	154	163
19		930	941	020	032	134	146
20		910	924	1.00000	1.00015	114	129
21		889	906	0.99979	0.99996	093	111
22		867	887	957	977	071	092
23		844	867	934	957	048	071
24		820	846	911	937	025	051
25		796	825	886	915	1.00000	029
26		770	802	860	892	0.99974	1.00006
27		744	779	834	869	948	0.99983
28		717	754	807	844	921	958
29		689	729	779	819	893	934
30		661	704	751	794	864	908

If we compare the normalities at the extreme temperatures for each of the standard temperatures, as reproduced in Table 17, it may be easily seen that the solutions, as to the change of the normality with temperature, may be divided into three groups.

TABLE 17.

Standard temp.	15°		20°		25°	
Solution.	5°	30°	5°	30°	5°	30°
Sodium hydroxide . . (n)	1·00245	0·99508	1·00393	0·99655	1·00550	0·99819
Sodium carbonate . . („)	230	521	374	664	534	820
Nitric acid („)	227	516	371	658	534	822
Sulphuric acid („)	221	516	356	659	526	818
Oxalic acid („)	1·00160	0·99580	1·00279	0·99698	1·00422	0·99840
Hydrochloric acid . . („)	153	608	264	718	395	849
Sodium chloride (1/10-n)	1·00108	1·99642	1·00201	0·99735	1·00321	0·99854
Silver nitrate („)	105	640	202	737	321	856
Amm. thiocyanate . . („)	104	639	199	734	322	856
Potas. permanganate. („)	096	643	193	737	312	856
Sodium carbonate . . („)	095	675	177	757	287	866
Oxalic acid („)	078	674	161	757	270	866
Sodium chloride (1/100-n)	089	649	178	738	295	853
Silver nitrate („)	089	655	177	743	294	858
Potas. permanganate. („)	087	653	181	745	294	858
Water („)	083	661	174	751	288	864

As seen from Table 17, the normal solutions are to be divided into two groups according to the degree of change of the normality with temperature. In each group, the change of the normality with temperature for different solutions do not differ from one another more than 0·5%, but if we take the two groups together, the change of the normality may differ from one another more than 1%.

Table 18 represents the mean values of those of the two groups of the normal solutions. The greatest deviation of the values in this table from the corresponding values of each solution is 0·7%. Thus, this table may be used for all normal solutions, if an error less than 0·7% is disregarded.

As to the decinormal and centinormal solutions, the change of volume with temperature may be taken as equal among themselves and also to the pure water, without any greater error than 0·5%.

TABLE 18.
Normal Solutions.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1·0019	1·0016	1·0032	1·0029	1·0048	1·0044
6		18	15	32	28	46	43
7		16	15	29	28	44	42
8		15	13	28	25	42	41
9		13	11	26	24	41	39
10		11	09	24	22	39	38
11		09	08	22	21	38	36
12		07	06	20	19	35	34
13		05	04	18	17	32	32
14		02	02	16	15	30	30
15		1·0000	1·0000	13	13	28	28
16		0·9997	0·9998	11	11	25	26
17		95	96	08	09	23	24
18		93	94	05	07	20	21
19		90	91	03	04	18	19
20		87	89	1·0000	1·0002	15	16
21		84	86	0·9997	0·9999	12	14
22		81	83	94	96	09	11
23		78	80	91	94	06	09
24		75	78	88	91	03	06
25		72	75	85	88	1·0000	03
26		69	72	82	85	0·9997	1·0000
27		66	69	79	82	94	0·9997
28		63	66	75	79	90	94
29		59	63	72	76	87	91
30		56	60	68	73	83	88

TABLE 19.
Decinormal and Centinormal Solutions.

Temp.	Standard temp.	15°		20°		25°	
		I	II	I	II	I	II
5°		1·0010	1·0007	1·0019	1·0016	1·0030	1·0027
6		10	7	18	16	30	27
7		09	7	18	16	29	27
8		08	6	17	15	29	27
9		07	6	16	15	28	27
10		06	5	15	14	27	26
11		05	4	14	13	26	25
12		04	3	13	12	25	24
13		03	2	12	11	24	23
14		01	1	10	10	23	22
15		1·0000	1·0000	09	09	21	21
16		0·9998	0·9999	07	07	19	19
17		97	98	06	06	18	18
18		95	96	04	05	16	18
19		93	95	02	03	14	16
20		91	93	1·0000	01	12	15
21		89	91	0·9998	0·9999	10	13
22		87	89	96	98	08	11
23		85	87	93	96	06	09
24		82	85	91	94	03	08
25		80	82	88	91	1·0000	05
26		77	80	85	89	0·9997	1·0003
27		74	78	83	87	95	0·9998
28		72	75	80	84	93	95
29		69	73	77	82	90	93
30		65	71	74	79	86	90

Table 19 gives the mean values of all the decinormal and centinormal solutions. The values in this table differ from the corresponding values of each of the solutions by 0.3% in extreme cases. Thus, this table is sufficient for all solutions, more dilute than decinormal.

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